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C. F. CHAND

COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION, AND MODES
OF ASSAYING THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

BY

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Second Edition, Revised and Enlarged

VOLUME I

*INTRODUCTION, ALCOHOLS, NEUTRAL ALCOHOLIC DERIVATIVES,
SUGARS, STARCH AND ITS ISOMERS, VEGETABLE ACIDS, &c.*

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PREFACE.

THE cordial reception given to the first edition of my COMMERCIAL ORGANIC ANALYSIS encourages me to hope that the revised version, of which this volume is the first instalment, will be received with at least equal favour.

In preparing this volume for the press, I have spared no pains to correct errors or ambiguities existing in the first edition, and the information has been, as far as possible, brought up to the latest date. The changes and additions thus necessitated have been very considerable, and, in fact, there are very few pages of the book which remain wholly unaltered.

Besides supplementing the information previously given by the addition of the most recent facts and processes, I decided, after due consideration, on rearranging the subject-matter of the work, so that each volume should treat more especially of kindred products. Thus, the volume now presented is devoted chiefly to the consideration of bodies of the Fatty Series and of Vegetable Origin, and includes chapters on the ALCOHOLS, ETHERS and other NEUTRAL DERIVATIVES of the Alcohols, SUGARS, STARCH and its ISOMERS, and VEGETABLE ACIDS.

The Second Volume of the new edition will probably be in the hands of the printer by the time these words are read, and treats more especially of Coal-Tar Products and bodies of the Aromatic Series, including PHENOLS and their ACID and NEUTRAL DERIVATIVES, COLOURING MATTERS, &c.; and, for reasons of practical convenience, HYDROCARBONS generally, and the FIXED OILS and the Products of their Saponification. The TANNINS will also be considered in the Second Volume.

I propose to devote a Third Volume to the consideration of Nitrogenised Organic Substances, including CYANOGEN COMPOUNDS, ALKALOIDS and ORGANIC BASES, ALBUMINOIDS, &c., and hope to have this ready for the press by the time Volume II. appears.

I believe that this rearrangement of subject-matter will render the book more convenient for reference, while adapting each particular volume to the special requirements of certain users.

I take this opportunity of thanking collectively the considerable number of Chemists, many of whom are personally unknown to me, who have given me the benefit of their special experience, and by whose assistance the book has greatly profited.

I am also largely indebted to many Scientific and Technical Journals, and to certain kindred works dealing with Proximate Organic Analysis, for much of the information incorporated in the new edition.

ALFRED H. ALLEN.

SHEFFIELD, *May* 8*th*, 1885.

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CONTENTS.

INTRODUCTION.

PAGE

PRELIMINARY EXAMINATION OF ORGANIC BODIES, . . . 3

SPECIFIC GRAVITY, ... 4

Specific Gravity Bottle, 4; Sprengel's Tube, 5; Hydrostatic Balance, 5; Hydrometers, 5; Vapour Densities, 8.

OBSERVATIONS OF CHANGES OF PHYSICAL STATE, . . . 9

Melting and Solidifying Points, 9; Subliming Points, 10; Boiling Points, 11; Fractional Distillation, 12.

OPTICAL PROPERTIES, ... 15

Refraction and Dispersion, 15; Fluorescence, 15; Rotation of the Polarised Ray, 16: Construction of Polarimeters, 16; Specific Rotatory Power, 20.

ULTIMATE OR ELEMENTARY ANALYSIS, ... 23

Carbon and Hydrogen, 25; Nitrogen, 25; Chlorine, Bromine, and Iodine, 26; Sulphur, Phosphorus, and Arsenic, 27; Metals, 27; Oxygen, 28.

BEHAVIOUR OF ORGANIC BODIES WITH SOLVENTS, . . . 28

Exhaustion by Solvents, 28; Soxhlet's Tube, 29; Employment of Immiscible Solvents, 30.

BEHAVIOUR OF ORGANIC BODIES WITH REAGENTS, . . . 36

Normal Solutions, 36.

EXAMINATION FOR INORGANIC MATTERS, ... 37

Determination of Ash, 37; Poisonous Metals, 39.

ALCOHOLS.

PAG.

Definition of an Alcohol, ... 41

Methyl Alcohol, ... 41

Wood Spirit, 44; Assay of Wood Spirit, 45; Acetone, 47; Allyl Alcohol, 48; Methylated Spirit of Wine, 48; Detection of Methyl Compounds in Alcoholic Liquids, 50.

Ethyl Alcohol, ... 53

Absolute Alcohol, 54; Rectified Spirit of Wine, 56; Proof Spirit, 56; Commercial Alcohol, 58; Detection of Alcohol, 59; Determination of Alcohol, 61; Tables of Densities of Diluted Alcohol, 62.

Alcoholic and Fermented Liquors, ... 74

Vinous Fermentation, 74; Wine, 77; Cider and Perry, 89; Malt Liquors, Beer, Ale, 90; Original Gravity of Worts, 98; Spirits, 102; Liqueurs or Cordials, 110; Tinctures, 111.

Amyl Alcohol, ... 114

Fusel Oil, 116; Detection of Amyl Alcohol in Spirituous Liquids, 119.

NEUTRAL ALCOHOLIC DERIVATIVES.

Ether, ... 123

Commercial Ether, 124; Methylic Ether, 127.

Compound Ethers, ... 128

Tabular List of Compound Ethers of Commerce, 129; Ethyl Acetate, 133; Ethyl Sulphates, 136; Xanthates, 137; Ethyl Nitrite, 138; Spirit of Nitrous Ether, 139; Ethyl Chloride, 155; Ethyl Bromide, 157; Amyl Acetate, 157; Amyl Nitrite, 158; Artificial Fruit Essences, 162.

Aldehydes, ... 163

Formic Aldehyde, 166; Acetic Aldehyde, 166.

Chloral, ... 170

Chloral Alcoholate, 171; Chloral Hydrate, 171; Butyric Chloral, 175.

Chloroform, ... 176

Commercial Chloroform, 178; Methylene Dichloride, 183; Bromoform, 184; Iodoform, 185.

SUGARS.

PAGE

Constitution and Classification of Sugars, ... 187

Tabular List of Sugars, 188; Saccharoids, 189; Glucoses, 190; Saccharoses, 192; Isolation of Sugars, 194.

Relations of the Sugars to Polarised Light, . . . 194

Specific Rotatory Power of Sugars, 194; Polarimetric Determination of Sucrose in the absence of other Optically Active Bodies, 199; Clerget's Process, 204; Polarimetric Determination of Sugars other than Sucrose, 208.

Specific Gravity of Saccharine Solutions, ... 209

Calculation of the Strength of Saccharine Solutions from the Density, 211; Table of Densities of Cane Sugar Solutions, 212; Saccharometers, 213.

Action of Strong Acids on Sugars, ... 214

Action of Nitric Acid, 214; Action of Concentrated Sulphuric Acid, 215.

Action of Dilute Acids on Sugars; Inversion, . . . 215

Fermentation of Sugars, ... 218

Action of Yeast, 218; Detection of a Fermentable Sugar, 218; Lactous Fermentation, 220.

Action of Alkalies on Sugars, ... 221

Saccharin, 222.

Reactions of the Sugar as Reducing Agents, . . . 223

Reaction of Sugars with Cupric Salts in Alkaline Solution, 223; Fehling's Copper Solution, 224; Reaction of Sugars with Solutions of Mercury, 229; Influence of Variable Conditions on the Reducing Power of Sugar Solutions, 231.

Recognition of the Principal Kinds of Sugar, . . . 233

Table showing Reactions of Sugars, 234; Values of K and S for the Principal Sugars, 236.

Cane Sugar. Sucrose, ... 238

Detection and Determination of Cane Sugar, 243; Commercial Sugar, 244; Sugar Confectionery, 255; Molasses or Treacle, 256; Sugar Cane and Beet Juices, 259; Valuation of Cane and Beet Products, 261.

PAGE

MALT SUGAR. MALTOSE, ... 263

Malt, 266; Chemical Examination of Malt, 268; Analysis of Malt Worts, 272; Malt Extract, 276.

MILK SUGAR. LACTOSE, ... 279

Determination of Milk Sugar, 281.

GLUCOSES, ... 284

Detection and Determination of Glucoses, 284; Dextrose, 287; Lævulose, 289; Invert Sugar, 292; Galactose, 292; Commercial Glucose or Starch Sugar, 293; Gallisin, 295; Honey, 307; Glucosides, 312.

STARCH AND ITS ISOMERS.

TABULAR LIST OF ISOMERS OF STARCH, ... 315

CELLULOSE, ... 316

Hydrocellulose, 317; Oxycellulose, 318; Composition and Analysis of Woody Tissues, 321; Recognition of Vegetable Fibres, 324; Cellulosic Nitrates, 326; Gun Cotton, 330.

STARCH, ... 331

Structure of Starch Corpuscles, 332; Microscopic Characters of Starches, 333; Detection and Determination of Starch, 341; Commercial Starch, 345.

DEXTRIN, ... 346

Commercial Dextrin, 348.

GUMS, ... 349

Tabular List of Principal Gums and Pectous Matters, 350; Gum Arabic, 351; Gum Tragacanth, 355.

PROXIMATE ANALYSIS OF PLANTS, ... 356

Tabular Scheme for the Analysis of Plant Products, 357.

COMPOSITION OF CEREALS, &C., ... 361

Albuminoids of Cereals, 362; Mineral Constituents of Cereals 367; Adulterations of Flour and Bread, 369.

ACID DERIVATIVES OF ALCOHOLS AND VEGETABLE ACIDS.

PAGE

REACTIONS OF VEGETABLE ACIDS WITH REAGENTS, ... 378

ACETIC ACID, ... 379
Reactions of Acetic Acid and Acetates, 381; Pyroligneous Acid, 384; Commercial Acetic Acid, 385; Glacial Acetic Acid, 386; Vinegar, 387; Potassium Acetate, 394; Sodium Acetate, 394; Ammonium Acetate, 395; Calcium Acetate, 395; Commercial Acetate of Lime, 395; Magnesium Acetate, 399; Aluminium Acetate. 400; Iron Acetates, 400; Black Liquor, 400; Lead Acetates, 401; Cupric Acetates, 402; Verdigris, 403.

HOMOLOGUES OF ACETIC ACID, ... 404
Properties of Lower Fatty Acids, 404; Formic Acid, 412: Propionic Acid, 413; Butyric Acid, 414; Pentoic or Valeric Acid, 415; Commercial Valerianates, 417.

LACTIC ACID, ... 418
Commercial Lactic Acid, 421; Lactates, 421.

OXALIC ACID, ... 423
Toxicological Examination for Oxalic Acid, 427; Commercial Oxalic Acid, 428; Oxalates, 429.

SUCCINIC ACID, ... 429
Commercial Succinic Acid, 431.

MALIC ACID, ... 432

TARTARIC ACID, ... 435
Detection and Determination of Tartaric Acid and Tartrates, 437; Commercial Tartaric Acid, 439; Tartaric Acid Liquors, 439; Lees, Argol, 442; Cream of Tartar, 443: Metallic Tartrates, 446; Potassium Hydrogen Tartrate. 446; Rochelle Salt, 448; Seidlitz Powders, 448; Potassium Ferric Tartrate, 448; Tartar Emetic, 449; Calcium Tartrates, 449; Cupric Tartrate, 451.

CITRIC ACID, ... 452
Detection and Determination of Citric Acid and Citrates, 453; Commercial Citric Acid, 455; Citric Acid Liquors, 458; Lemon and Lime juice, 458; Metallic Citrates, 463; Lithium Citrate, 464; Calcium Citrate, 464; Magnesium Citrate, 465; Ferric Citrate, 465; Bismuth Citrate, 466.

ERRATA, ... 466

INDEX, ... 467

INTRODUCTION.

1. The term Analysis, though originally meaning the separation or splitting up of a substance into its constituent parts, has now become greatly extended in its application, so that a process of chemical analysis may mean either—

a. A true analysis, or separation of a substance into its constituent parts;

b. A qualitative identification or recognition of a substance sought for; or

c. A quantitative determination, with more or less accuracy, of the amount of a particular body.

When the quantitative determination is limited to one or two important bodies which constitute the valuable or active constituents of a more complex substance, the analytical process is frequently called an *assay*. It is in this sense the term assay is employed throughout this work.

2. Very frequently the chemical examination of a substance includes the search for, or determination of, impurities and foreign constituents accidentally present or purposely added. The nature of the foreign ingredients will, of course, largely depend upon that of the substance, and cannot be generally described. They may, however, be conveniently classified under the following heads:—

a. Foreign bodies naturally associated with the main substance, and not readily removed during the process of preparation. *Examples:* acetone in wood spirit; hydrocyanic acid in bitter-almond oil; and cresylic acid in carbolic acid.

b. Foreign bodies introduced during the process of manufacture, and not subsequently (perfectly) eliminated. *Examples:* cyanate and carbonate of potassium in commercial cyanide; sulphuric acid and lead in organic acids; alcohol in ether.

c. Foreign bodies legitimately added in small quantity, to confer some special property on the main substance. *Examples:* mineral acids in hydrocyanic acid; alcohol in chloroform.

d. Foreign bodies produced by the spontaneous change of the main substance. *Examples:* benzoic acid in bitter-almond oil; metaldehyde in aldehyde; ethyl acetate in tincture of acetate of iron.

e. Adulterants purposely added to increase the weight or bulk, to confer some special property, or to conceal weakness or inferiority of the main substance. *Examples:* water in spirituous and vinous liquids; tartaric acid in citric acid; nitro-benzene in bitter-almond oil.

3. For the physical and chemical examination of organic bodies a great variety of methods are employed, the details of which will be given under the proper heads, but the following general principles are frequently employed for the recognition and quantitative examination of organic bodies:—

a. A *preliminary examination* of the leading characters of the body, such as its colour, taste, odour, microscopic appearance, and crystalline form.

b. A determination of the *specific gravity* of the body, sometimes in the solid form, more frequently in the liquid condition, and occasionally in the state of vapour. The density of the solution of a substance is often a character of value.

c. Observations and operations connected with a *change in the physical state* of the substance, such as determinations of its melting and boiling point, and its behaviour on distillation.

d. A study of the *optical properties* of the substance, including its refractive and dispersive powers, absorption-spectrum, fluorescence, and action on a ray of polarised light.

e. A determination of the ultimate or *elementary composition* of the body.

f. The behaviour of the substance with ordinary *solvents.*

g. The behaviour of the substance with other *reagents.*

h. An examination of the substance for *inorganic matters.*

The foregoing methods of examination are chiefly applicable to the recognition of comparatively pure substances, but the principles involved are continually employed in the practical proximate analysis and chemical examination of organic bodies. Thus, by the varied behaviour of the associated bodies, when examined by one or more of the above methods, we effect a practical recognition, determination, or separation of the constituents of the sample.

It is not proposed to describe the whole of the above methods of examination in detail, as many of them are procedures with the general nature of which the user of this book is presumably acquainted. In most cases, the outline of the method of examination is alone indicated, but exceptions are made in cases in which the same methods are not in general use in the analysis of inorganic substances. Sufficient working details for the use of any one versed in simple chemical manipulation are given under the special articles devoted to the examination of the various organic preparations employed in commerce.

PRELIMINARY EXAMINATION.

4. When the organic body to be examined is of wholly unknown nature, a judicious preliminary examination will often throw much light on its composition. The following points should not be lost sight of:—

Colour.—The colours of organic bodies are not as a rule very characteristic, but there are some very remarkable exceptions. As a rule, blue vegetable colouring matters are rendered red by acids, and the blue colour is restored or changed to green by ammonia. Indigo is not affected. Vegetable yellows are generally turned brown by alkalies, and the colours restored by acids. The examination of the absorption-spectra of coloured organic substances often furnishes most valuable information.

Taste.—This character must be observed with extreme caution, as many organic bodies are intensely poisonous. The safest way is to make a weak aqueous or alcoholic solution of the substance, and taste a drop of the liquid cautiously. Acids are, as a rule, sour or astringent in taste. Alkaloids are usually bitter. The sugars and glycerin are sweet.

Odour.—The smell of organic compounds is often highly characteristic, and notably so in the case of the neutral alcoholic derivatives.

Microscopic Appearance.—In the case of solid bodies an examination under the microscope is often extremely useful. As a rule, the use of a high power is neither necessary or desirable. The micro-polariscope affords a valuable means of identifying the starches.

Crystalline Form.—This character is often of great service for the recognition of organic bodies, but is rarely a test of their purity. In the great majority of cases the crystals are too small or indistinct to admit of any goniometric determination, though the action of polarised light may frequently be observed. Instances of the value of crystalline form as means of identification are to be found in the cases of cholesterin, salicylic acid, tartaric acid, and some of the alkaloids and their salts.

Effect of Heat.—The behaviour of organic substances on heating is often highly characteristic. Solids should be heated in a small dry test-tube. It is well to make an experiment first on a piece of platinum foil, as a few substances explode violently when heated. On ignition in the air all organic substances other than those containing metals are completely consumed. Sometimes volatilisation occurs without darkening; in other cases, a more or less voluminous residue of carbon is left, which is sometimes only burnt away with great difficulty. Salts of organic acids containing metals of the alkalies or alkaline earths usually leave these metals as carbonates on being ignited in the air. Hence the presence of carbonate in the ash indicates the previous presence of an organic acid. Volatile heavy metals, such as arsenic or mercury, are wholly driven off on igniting substances containing them, but most heavy metals remain on ignition either as oxides or in the metallic state.

The density, boiling and melting points, and other physical properties of the substance may be roughly noted as part of the preliminary examination, but these characters are referred to at greater length in the following sections.

SPECIFIC GRAVITY.

5. The density of an organic solid or liquid is often a most valuable criterion of its identity or purity. Unlike the determination of the density of a vapour it is frequently applicable to the accurate estimation of a substance in solution or in admixture with another body, and in other cases it may be used to discriminate between different isomeric bodies of the same percentage composition.

The specific gravity of a solid or liquid is generally referred to water taken either as *unity* or as 1000. Both plans have their advantages, and, as no confusion can arise from such a course, the densities given in this work will be stated in either manner, according to convenience of expression or comparison.

6. **The Specific Gravity Bottle** is the most generally serviceable means of taking the densities of solids and liquids. It should not be trusted to contain the amount of water marked on it, but should be carefully filled with distilled water at the temperature at which the sample of liquid is to be compared (usually 15°·5 C. = 60° F.), and the weight of contained water ascertained. The density of the sample of liquid is found by dividing the weight of it which the bottle will contain by the weight of water contained at the same temperature. When the liquid is miscible with water, the wet bottle may be rinsed out once or twice with a few drops of

the sample; when the liquid is insoluble or nearly so in water, the bottle should be rinsed once or twice with alcohol and then with ether, the last traces of the latter being got rid of by a current of dry air from a bellows, or by sucking the ether vapour from the warmed bottle by means of a glass tube.

7. **Sprengel's Tube.**—A very useful and accurate method of taking the specific gravity of liquids, especially when but small quantities of material are at disposal, is by a method described by H. Sprengel (*Jour. Chem. Soc.*, xxvi. 577), in which a small U-shaped apparatus terminating in horizontal capillary tubes is substituted for the ordinary specific gravity bottle. It may be filled with liquid with extreme ease, and the regulation of the quantity of contained liquid is also very easily effected. The results are extremely accurate. Sprengel's tube has the advantage that it can readily be used for ascertaining the density of liquids at the boiling point of water. This is important in the case of substances which are solid at the ordinary temperature.

8. **Mohr's Hydrostatic Balance** is a very convenient instrument for many purposes. A thermometer suspended from a piece of platinum wire is attached to one end of a counterpoised lever. On immersing the thermometer in a liquid it loses a certain weight. The equilibrium is restored by hanging riders on the lever, the weight required being that of a quantity of the liquid equal in measure to the immersed thermometer. The series of riders are adjusted in weight so as to make the reading very simple. In making an observation, counterpoise is effected when by the addition of riders the beam remains in a horizontal position.

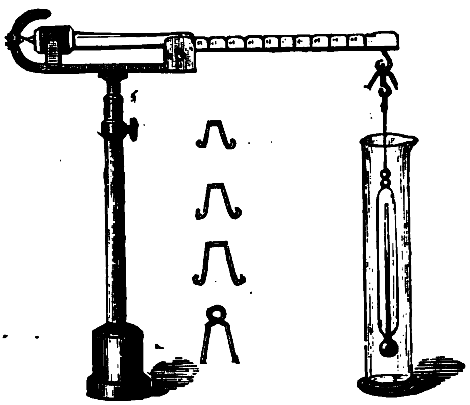

Fig. 1.

9. **Hydrometers** are instruments the use of which is too well known to require detailed description. Care should be taken, in accurate observations, to read either from the top, bottom, or centre of the meniscus, according to the manner in which the instrument is graduated. Attention should also be paid to the temperature of the liquid during the observation.

The graduation of hydrometers, even when sold by well-known firms, is often far from accurate; and hence the indications of such instruments should be carefully verified.

The accuracy of hydrometer-densities has been questioned in the case of milk and other liquids containing suspended particles, but the experiments of L. Siebold (*Analyst*, iv. 189) show that the indications of the hydrometer in such cases agree with those obtained by the specific gravity bottle.

10. **Twaddell's Hydrometer** is applicable only to liquids heavier than water. The indications are translated into actual densities by multiplying the degrees Twaddell by 5, and adding 1000. Thus a liquid which marks 68° Twaddell has an actual density of $(5 \times 68) + 1000 = 1340$, compared with water as 1000.

11. **Baumé's Hydrometer** is not commonly used in England, except for ascertaining the density of saccharine solutions. As originally constructed, the point to which the instrument sank when immersed in a solution of 15 parts of dry common salt in 85 parts by weight of water was taken as 15 degrees. The interval between this point and that at which the hydrometer stood when immersed in pure water was divided into 15 equal parts, and a scale of similar equal parts extended as far as was necessary. Francœur found the density of a solution of common salt of the above strength to be 1109; Soubeiran, 1116; Gerlach, 1114; while Coulier gives 1110·725. The subject has been investigated by Baudin (*Chem. News*, xxi. 54), who found the density to be 1111 at 15° C.

According to Baumé's original scale, concentrated sulphuric acid of 1845 specific gravity marked 69½ degrees. Gay Lussac proposed a modified scale, according to which the same density corresponded to 66 degrees at 15° C. Of late years, all the Baumé hydrometers made in England[1] appear to have been graduated on a scale intermediate between these two (G. W. Wigner, *Analyst*, v. 138).

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[1] In America, Baumé hydrometers for liquids heavier than water are graduated by taking water at 15° C. as the zero point, and sulphuric acid of 1842·7 specific gravity at 15° C. as equal to 66° Baumé. This gives the following formula for calculating actual densities:—

$$\text{Sp. gr.} = \frac{144{,}300}{144{\cdot}3 - \text{deg. B.}}$$

For liquids lighter than water the formula is as follows:—

$$\text{Sp. gr.} = \frac{146{,}000}{136 + \text{deg. B.}}$$

That such an instrument as Baumé's hydrometer should ever have come into general use is a serious misfortune, but that its indications should be different in England and America is discreditable to both countries.

On such instruments, a liquid of 1480 specific gravity marks 48 degrees Baumé, and hence the actual specific gravity may be calculated by the following formula—

$$\text{Sp. gr. (water} = 1000) = \frac{148{,}000}{148 - \text{deg. B.}}\ ^{1}$$

Thus, if a liquid mark 12° Baumé the actual specific gravity will be 1088·2; for

$$\frac{148{,}000}{148 - 12} = 1088{\cdot}2.$$

Baumé's hydrometer *for liquids lighter than water* is graduated by taking pure water as 10°, and the zero is found by immersing the instrument in a solution of 10 parts of common salt in 90 of water. The indications may be calculated into degrees of real density by the formula—

$$\frac{140{,}000}{130 + \text{deg. B.}} = \text{specific gravity}.^{1}$$

12. **Cartier's Hydrometer.**—22° corresponds with 22° Baumé, but above and below this point the degrees are diminished in the ratio of 16 to 15.

13. **Beck's Hydrometer.**—The zero point corresponds to the density of water, and 30° to a density of 850, the scale being divided into equal parts above and below the zero point, as far as desirable.

Other hydrometers are described in the section treating of the "density of saccharine solutions."

14. Unfortunately, much confusion has crept into the mode of stating specific gravities. Thus, if a liquid be stated to have a density of ·7185 at 17°·5 C., there is really no certainty as to what is intended to be understood by the statement. It may be meant that a bottle which held 100 grammes of water at 17°·5, held only 71·85 grammes of the liquid. Or the bottle may have held 100 grammes of water at 15°·5 C. (= 60° F.), at 15°·0 C., at 4°, or at 0° C. In many instances it is quite uncertain whether the recorded densities refer to a comparison with an equal bulk of water at the same temperature as that at which the liquid was weighed, or at any one of the temperatures just given. As a rule, when the density of a substance is stated to be so much at 15°·5 C. (= 60° F.), it may be regarded as certain that the unit of water was weighed at the same temperature, but in the other cases it is by no means certain what is meant. This fertile source of error

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[1] See footnote on last page.

has been commented on in an able manner by W. A. Tilden. (*Chem. News*, xxxviii. 300).

15. The specific gravity of *organic solids* is best taken by introducing some fragments or powder into a specific gravity bottle and ascertaining the weight taken in grammes. The bottle is next filled with water, petroleum, or some liquid of known density having no solvent action on the solid to be examined, and the weight is then again observed. The increase gives the weight of contained liquid, and this, multiplied by its known density, gives its volume. This subtracted from the known capacity of the bottle in c.c. gives the measure of the solid, which, divided into its weight in grammes, gives the density compared with water as unity. Care must be taken to avoid the adherence of air-bubbles to the solid. Agitation will generally suffice to get rid of them.

Hager has described (*Analyst*, iv. 206) a method of ascertaining the specific gravity of fats and similar bodies, by diluting alcohol or strong ammonia with water until suspended fragments of the substance remain in equilibrium in any part of the liquid at a temperature of 15°·5 C. The density of the liquid is then taken, and is clearly identical with that of the suspended solid.

16. **Vapour-Densities.**—The determination of the vapour-density of an organic body often furnishes a most complete test of its formula. In all cases in which no decomposition of the substance occurs, the density of the vapour, compared with that of hydrogen at the same temperature and pressure, is *one-half* the molecular weight.

Thus the density of the vapour of alcohol is 23 times that of hydrogen, which gives 46 as the molecular weight, and establishes the formula C_2H_6O. Similarly, benzene vapour is 39 times heavier than hydrogen, which corresponds with the formula C_6H_6, and negatives the possibility of CH, C_2H_2, or other simpler formula expressing the true constitution of benzene.

17. The determination of vapour-densities is more frequently of service in original organic research than in the examination and assay of commercial organic products, and it is, therefore, unnecessary to describe in detail the various methods of making such observations. A very simple and convenient apparatus for taking vapour-densities is, however, shown on next page (fig. 2). It is due to V. Meyer (*Deut. Chem. Ges. Ber.*, xi., 1867 ; and *Jour. Chem. Soc.*, xxxvi. 177), and consists of a sort of cylindrical flask, with a very elongated neck provided with a side tubulure. The flask is placed in an outer tube, which is filled with some liquid heated to a somewhat higher temperature than the boiling point of the substance of which it is desired to ascertain the vapour-density.

A cork is inserted in the mouth of the flask, and the orifice of the side tubulure is brought under the water of a pneumatic trough. As soon as the temperature becomes constant, as indicated by no further expansion of the air taking place, the cork is removed from the flask, a weighed quantity of the substance dropped in, the cork quickly replaced, and a graduated cylinder filled with water placed over the orifice of the gas-delivery tube. In fifteen to twenty seconds, air collects in the cylinder in volume equal to that of the vapour formed by the volatilisation of the substance introduced. In practice, the weighed quantity of the substance should be contained in a small thin tube, which should be allowed to drop on a cushion of asbestos or glass-wool arranged at the bottom of the flask. Watson Smith (*Jour. Chem. Soc.*, xxxvii. 491), who has materially improved the manipulation with Meyer's apparatus, employs an arrangement by which the removal of the cork is avoided, and the tube is detached from its under side after the cork is in position.

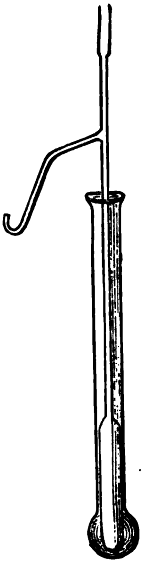
Fig. 2.

When no more bubbles collect in the graduated cylinder it is removed to a larger cylinder filled with water, the internal and external liquids brought to the same level, and after a time the volume of the air (V) read off, the temperature of the water (t), and the height of the barometer being at the same time observed, and corrected for a temperature of 0° C. The figure thus obtained is called B, and if the weight of the substance used be S, and the tension of the vapour of water at the temperature of the air w, the vapour-density of the substance may be found from the following equation :—

$$\text{Vapour-density} = \frac{S(1 + 0{\cdot}003665\,t) \times 587780}{(B - w)V}.$$

OBSERVATIONS OF CHANGES OF PHYSICAL STATE.

18. **The Melting Point** or **Solidifying Point** of an organic body can be determined by means of the apparatus described for taking subliming points (par. 20), the glass ring and upper disc being omitted. In some cases it is preferable to place the substance directly on the mercury. Several determinations can be made simultaneously by this method. For readily

fusible bodies, the porcelain crucible should be substituted by a beaker placed in another beaker containing iced water or a freezing mixture. On removing the bath containing the cooling agent the temperature of the mercury gradually rises, and the temperature at which the substance under examination melts can be observed with great accuracy. In taking the melting points of less fusible substances there is no occasion to cool the mercury, which, on the contrary, is immersed in a beaker filled with water to a higher level than the mercury. The water is heated *very* gradually till the substance becomes transparent or gives other signs of liquefaction. For still less fusible substances a non-volatile liquid must be substituted for the water.

19. The foregoing method, devised by T. Redwood, is applicable within an extensive range of temperature, but in some respects the following plan is preferable. The substance is melted at a temperature slightly above its fusing point, and while molten is sucked up into a very narrow glass tube, where it is allowed to solidify. After an interval of not less than one hour the tube is attached by a cork or india-rubber ring to the stem of a thermometer, in such a manner that the part of the tube containing the substance of which the melting point is to be observed, shall be at the same level as, and in close proximity to, the bulb. The thermometer with its attached tube is then immersed in water, or other transparent liquid having no solvent action on the substance under examination, and the water is gradually heated until fusion of the contents of the capillary tube takes place, when the thermometer is observed and the temperature recorded as the melting point required.

20. **The Subliming Point** of an organic body is sometimes an important characteristic, but its value depends much on the manner of making the observation. A. Wynter Blyth recommends the following method:—A porcelain [crucible about three inches in diameter is nearly filled with mercury (or, for high temperatures, fusible metal). A minute quantity of the substance to be examined is placed on a thin disc of microscopic covering glass, which is floated on the mercury, and covered with a glass ring (cut from tubing) on which is placed a second disc so as to form a closed shallow cell. The porcelain crucible is placed on a brass plate and covered with a flask from which the bottom has been removed. This serves to keep away currents of air, and supports the thermometer, which passes through a cork in the neck, so that the bulb is immersed in the mercury. In the first examination of a substance the temperature is raised somewhat rapidly, the upper disc being removed by forceps and exchanged for

a fresh disc at every rise of 20 degrees, until the substance is destroyed. A second determination is conducted more slowly and the discs more frequently changed, while in conducting the third determination the heat is raised very cautiously, and the discs changed every half degree when the previously ascertained subliming point is nearly reached. Blyth defines the subliming point as the lowest temperature, which, if maintained for 60 seconds, allows of the formation of the most minute dots, films, or crystals which can be observed by a microscopic power of ¼ inch.

The great majority of subliming points given in this work have not been determined in the above exact manner.

21. **Observation of the Boiling Point.**—In making this important determination it is necessary to remember that a boiling liquid is often several degrees hotter than the vapour rising from it. In observing the boiling point, therefore, care must be taken that the thermometer bulb is not immersed in, but is situated slightly above, the surface of the liquid, which should be caused to boil rapidly. The liquid may be contained in a simple test-tube fitted with a cork carrying the thermometer and a short open tube for the escape of the vapour. A small tubulated flask or retort may be substituted for the test-tube. When the quantity of the liquid at disposal is only small, the test-tube should be thin and immersed in a flask half filled with glycerin, paraffin, sulphuric acid, or other suitable liquid. On heating the contents of the flask, the thermometer fitted to the test-tube continues to rise till the boiling point of the liquid is attained, when it remains stationary till the latter has evaporated. A very small quantity of liquid (½ to 1½ c.c.) suffices for the determination of the boiling point in this manner.

22. In accurate determinations of boiling points, attention must be paid to the barometric pressure at the time, and the errors to which the thermometer is itself liable must not be neglected. For practical purposes, any change in ordinary atmospheric pressure may be assumed to affect the boiling points of all liquids to an equal extent. This may be taken as 0°·1 C. for a variation in the pressure of 2·7 millimetres (=about 0·1 inch) of mercury. Thus water boils at a temperature of 100° C. under the standard pressure of 760 mm., but if the barometer fall to 733 mm. the boiling point will be reduced to 99° C.

23. Distillation is a process of which there is no occasion to give a detailed description. For cooling the vapour some form of Liebig's condenser is commonly employed. A useful modification, by which distillation can be made at once to succeed

digestion, without rearrangement of the apparatus, has been described by W. A. Shenstone (*Jour. Chem. Soc.*, xliii. 123).

24. Fractional Distillation is an analytical process closely related to the determination of the boiling and subliming points of organic bodies, and by repeating the process, and collecting apart the fractions which distil at every small increase of temperature, very perfect separation may sometimes be effected.

25. When only a small quantity of a complex liquid is submitted to fractional distillation, it is better to keep the bulb of the thermometer wholly immersed in the liquid, as the error liable to be caused by this arrangement is far less than ensues, especially towards the end of the distillation, from the temperature of the residual liquid rising more rapidly than the thermometer can acquire the temperature of the vapour.

26. In conducting a fractional distillation, it is desirable to operate on a known weight or measure of the substance, and to note the proportion of the whole which passes over at every few degrees of rise in the temperature of the distilling liquid. Details of the precautions which should be taken to ensure constant results will be found in the section treating of the assay of commercial benzols.

27. Fractional distillation is a process of the utmost value for effecting the proximate analysis of mixed organic substances of various boiling points. Speaking generally, the first portions which distil will contain the greater part of the more volatile constituents of a complex fluid, but the composition of the distillate at various stages of the process depends on many circumstances besides the boiling points and relative proportions of the constituents of the mixture operated upon.

28. Wanklyn first showed that the proportion in which the constituents of a mixture pass over depends not only on their relative abundance in the mixture undergoing distillation, and on their respective vapour-tensions at the temperature of ebullition, but also on their mutual adhesion, and on the densities of their vapours. He found that, when a mixture of equal weights of two liquids of different boiling points was distilled, the quantity of each constituent in the distillate was proportional to the product of its vapour-density and vapour-tension at the temperature of ebullition of the fraction. Hence, in certain cases, the less volatile of two substances may pass over most rapidly—that is, be found in largest quantity in the first fraction of the distillate. This is true of a mixture of methyl alcohol (boiling at 65°·2) and ethyl iodide (boiling at 72°). If the vapour-tensions and vapour-densities of the two liquids are inversely proportional, the mixture will distil unchanged.

29. Carea Lea found that, on distilling a mixture of the hydrochlorides of ethylamine, diethylamine, and triethylamine with caustic alkali, the whole of the last amine, which is the least volatile of the three, was contained in the first portions of the distillate, provided that its proportion was not excessive. A similar anomaly is observed on distilling solutions of acetic acid and its homologues.

30. Sometimes anomalous results ensue, owing to the fact that the tension of the mixed vapours is never equal to the sum of the tensions of the individual vapours. Berthelot found that if a mixture of 90·9 parts carbon disulphide (boiling at 46°·6), with 9·1 alcohol (boiling at 98°·4), were distilled, it behaved as a homogeneous liquid. If either of the constituents were present in excess of the above proportion, it remained in the retort in an unmixed condition after the definite mixture had distilled over. Thorpe, again, found that a mixture of equal volumes of methyl alcohol and carbon tetrachloride distilled at a temperature nearly 10° lower than that of the boiling point of the most volatile constituent, and the carbon tetrachloride, which has the higher boiling point, occurred most largely in the first fractions of the distillate.

31. In cases where two immiscible liquids are distilled together, the boiling point is the temperature at which the sum of the vapour-tensions is equal to the atmospheric pressure. Thus benzene and water distil together at 69°·1, at which temperature benzene vapour has a tension of 533·7 mm., and steam 224·2 mm., the sum of the two being 757·9 mm.

32. A valuable series of papers on the theory and practice of fractional distillation have been published by F. D. Brown (*Jour. Chem. Soc.*, xxxv. 547; xxxvii. 49.; and xxxix. 304, 517).

33. From a consideration of the foregoing facts it will be evident that a complete separation of a complex liquid into its constituents is never possible by a single fractional distillation, and that in certain cases it is impossible even by repeating the operation a very great number of times.

34. A great improvement in the practice of fractional distillation was made by Warren, who, in his researches on American petroleum, employed a Liebig's condenser inclined towards the distilling flask, and kept at such a temperature as to cause condensation of the less volatile constituents of the mixed vapour, while those of lower boiling point passed on to a condenser kept cool in the usual way, and inclined in a direction opposite to the first.

35. Various arrangements have been devised by which the

vapour of the distilling liquid is partially condensed, and succeeding portions are caused to be washed with the liquid produced, which periodically runs back into the distilling flask. A very useful arrangement of this kind is that of Le Bel and Henninger (fig. 3), which consists of a number of bulbs, varying from two to six, blown upon a tube, which is fitted by means of a cork into the mouth of the flask containing the liquid to be distilled. The upper end of the tube is furnished with an inclined side-tube, which can be fitted by a cork to a Liebig's condenser, and with an orifice through which a thermometer can be passed, so as to observe the temperature of the vapour which passes over. Each of the bulbs is connected with the one below by means of a small side-tube. In the constriction of each bulb is placed a small cup of platinum or copper gauze, of the size and shape of a small thimble. These cups are made by folding the gauze over the end of a stout glass rod. The ascending vapour condenses in the cups, and thus serves to wash the vapour subsequently formed, as it bubbles through. When the liquid rises to a certain height in each bulb it runs off by the side-tube, and ultimately finds its way back to the distilling flask, the flame of which is so regulated as to keep all the cups full, and cause the distillate to fall from the end of the tube in separate drops. In an improved form of dephlegmator, devised by Glynsky (fig. 4), the wire gauze is replaced by hollow balls of glass, introduced into the bulbs during manufacture.

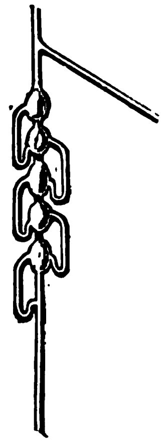
Fig. 3.

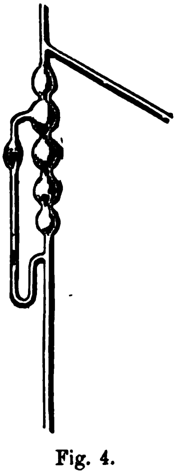
Fig. 4.

36. Hempel (*Jour. Chem. Soc.*, xlii. 551) substitutes for the more complex arrangement a long wide glass tube, arranged vertically and filled with solid glass beads. By this contrivance he obtained alcohol of 95 per cent. by slowly distilling spirit of 18 per cent.

37. L. T. Thorne (*Jour. Chem. Soc.*, xliii. 301) has described an apparatus for fractional distillation under reduced pressure which allows the distillate to be withdrawn, when desired, without interfering with the vacuum.

38. The subject of fractional distillation has been recently treated in an able paper by G. Lunge (*Chem. Zeit.*, I. 896).

OPTICAL PROPERTIES.

39. **Refraction and Dispersion of Organic Bodies.**—The specific refraction of many organic substances has been studied by J. H. Gladstone (*Phil. Mag.* [5], xi. 54), J. V. Janovsky, and others, but no practical application has been made of their observations.

40. **The Absorption-Spectrum** of an organic substance occasionally furnishes information not to be obtained in any other way, and in the examination of blood stains, dye materials, and other coloured substances is often of great utility.[1]

41. THE MICROSPECTROSCOPE.—For observing the absorption-spectra of organic substances, a pocket spectroscope will often suffice, but it is far better to employ a microspectroscope,[2] furnished with a proper comparison stage and reflecting prism, so as to allow of the spectrum of the colouring matter under examination being viewed in juxtaposition with the spectra of standard specimens of known origin.

42. **The Fluorescence** of organic bodies is often a qualitative character of much value. It is absolutely necessary that the liquid to be observed should be *perfectly clear*, as the pressure of minute suspended particles often causes the production of a spurious fluorescence which may lead to very fallaceous conclusions.

43. As a rule, the phenomenon of fluorescence may be observed by filling a small test-tube with the fluorescent liquid, holding it in a vertical position before a window, and observing the liquid from above against a dark background. Another plan is to make a thick streak of the liquid on a piece of polished jet or black marble, or on a glass plate smoked at the back,[3] and to place the streaked surface in front of, and at right angles to, a well-lighted window. Examined in this manner, very slight fluorescence is perceptible.

44. In some cases, the following method of observing fluorescence may be advantageously employed. A cell is made by

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[1] The researches of W. N. Hartley show that many colourless organic substances produce, in the ultra-violet portion of the spectrum, absorption-bands which are apparently dependent on the constitution of the substances (*Jour. Chem. Soc.*, xli. 45, and *Proc. Roy. Soc.*, cxxxi. 1). Similarly, Abney and Festing have proved the occurrence of absorption-bands in the ultra-red region. No practical application of these interesting and suggestive facts has hitherto been made.

[2] A very serviceable instrument is made by J. Browning, Strand.

[3] Either of these is infinitely superior to the polished tin plate usually recommended. In short, the background should be black, not white.

cementing a piece of barometer-tube about ¾ inch in length, and having an internal diameter of ⅛ inch, to a glass microscope-slide, by means of black sealing-wax. The open end of the cell must be well polished. On introducing a clear solution of any fluorescent substance, covering the cell with a piece of thin glass, placing the slide on the stage of a microscope, illuminating the tube at the side by means of strong daylight, and looking down and observing the axis of the cell by a low microscopic power, the liquid will appear more or less turbid, and of a colour dependent on the nature of the fluorescent substance in solution. If no fluorescent body be present, the field will appear perfectly black, as no light is reflected either from the apparatus or the liquid. When desired, the *spectrum* of the fluorescent light can be observed by the micro-spectroscope. In some instances the spectrum thus obtained shows remarkable and characteristic bands.

45. **Double Refraction,** as observed under the microscope by means of polarised light, is often of value for the recognition of organic bodies. In addition to the well-known phenomena dependent on crystalline form, many organic substances not actually crystallised exhibit a cross and series of rings when viewed by polarised light. This is notably the case with many of the starches, and furnishes a valuable means for their discrimination.

46 **Rotation of the Polarised Ray.**—Many organic substances possess the power of rotating the plane of polarisation of a luminous ray; and as this property is exerted even by the *solutions* of optically active substances, the angle through which the rotation occurs often serves for the accurate determination of certain bodies. The method is employed for the examination of saccharine matters, turpentine, certain alkaloids, &c.

47. CONSTRUCTION OF POLARIMETERS.—In all forms of apparatus for measuring the rotation of the plan of polarisation of a luminous ray, the polariser, or optical means of obtaining a beam of polarised light, consists of a double-refracting prism of calcite. In some cases a double-image prism is used, but in others the extraordinary ray only is employed. The analyser is composed of a single-image prism, and a Galilean telescope is frequently employed as an eye-piece. On rotating the analyser through 90° the field becomes perfectly dark, but on introducing between the analyser and polariser a tube filled with sugar solution, or other optically active liquid, the light again passes. If white light be used the transmitted tint varies with the strength of the solution of sugar and the length of the tube interposed, and rotation of the analyser merely causes an alteration in the colour of the transmitted light, a phenomenon due to the fact that rays of

differing refrangibility are rotated unequally. If monochromatic light be employed, a certain angular rotation of the analyser will suffice wholly to extinguish the light from the field of view, and hence, by measuring the angle through which the analyser must be rotated to restore darkness, an estimate of the strength of the interposed liquid in sugar or other active constituent may be obtained. Quartz is well known to possess very powerful rotatory action on polarised light, a plate 3·75 millimetres in thickness (=0·148 inch) rotating the plane of polarisation of the mean yellow ray through 90 degrees. Some specimens of quartz possess right-handed rotation, and others are *lævo*-rotatory to an equal extent. Hence, a double plate composed of equal thicknesses of the two varieties possesses no rotatory power. If a plate be composed of semicircles of right and left-handed quartz, each 3·75 millimetres in thickness, and such a plate be placed between the Nicol's prisms while their principal sections are parallel, the field becomes tinted of a peculiar purple, or corn-flower colour, known as the *teinte du passage* or transition tint. The least rotation of the analyser causes one-half of the circle to incline to red and the other half to violet, and the interposition of a tube of sugar solution or other rotating liquid produces a similar effect, while to restore uniformity of tint necessitates a rotation of the analyser through an angle dependent on the strength and thickness of the polarising liquid used.

48. M. Soleil has applied these principles in a very ingenious manner in his well-known saccharimeter, the construction of which is illustrated and described in Watts' *Dictionary of Chemistry*, and other standard works. The Soleil instrument, however, shares with all others dependent on an observation of the transition tint the disadvantage that the *teinte du passage* is not always the same for different eyes, and that the errors inherent in the construction of the instrument become greatly intensified if the solution under observation be not strictly free from colour.

49. In the case of coloured liquids, therefore, or in the event of the observer being somewhat colour-blind, it is far better to employ some instrument constructed for observation with the monochromatic sodium flame. In the polaristrobometer or shadow-polariscope of Wild, a Savart double plate of quartz is placed behind the analysing prism and the solution-tube; the field appears crossed by dark bands or striæ which can be caused to disappear by rotating the analyser, so that at the conclusion of the observation, or in the absence of an active rotating substance, the field appears uniform. The rotating power of the interposed liquid is read off on a divided circle.

50. In using this and other polarimeters employing monochromatic light, the source of illumination is a bunsen flame rendered luminous by inserting in it a loop of platinum wire holding a bead of sodium carbonate, or a platinum trough containing previously melted sodium chloride. An advantageous addition is a transparent plate of potassium bichromate fixed on the end of the instrument nearest to the flame.

Hofmann's saccharimeter is an instrument very similar to Wild's.

51. Laurent's polarimeter is one of the simplest and best. It is the instrument employed in the French Government laboratories for the analysis of sugar. One-half of the field of vision is covered by a very thin plate of quartz, which allows some of the light to pass, even when the analyser and polariser (both of which are Nicol's prisms) are crossed. If the analyser be rotated so as to cause the quartz plate to become dark, light passes through the uncovered half of the field. In a position intermediate between these two, the two halves of the field appear equally dark, and this is the zero point of the instrument. The slightest deviation from this neutral position causes one-half of the field to appear darker and the other half lighter than before. Hence, the change is a double one and the instrument very sensitive. Monochromatic light must be used. The more modern instruments have the divided circle graduated both in circular degrees and sugar units.[1]

52. In the Jellett-Cornu polarimeter the polariser is a peculiarly cut crystal of calcite known as a Jellett's prism, the analyser being a Nicol. At a certain position of the latter, the two halves of the field appear equally illuminated. Monochromatic light is used,[2] and the indications are read off on a divided circle.

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[1] As a rule, in the Wild, Laurent, and Jellett-Cornu polarimeters, one-half the circle is divided into circular degrees, the other half bearing a sugar-scale. Thus, the Jellett-Cornu instruments made by Duboscq have 100 divisions, of such size that by taking 16·350 grammes of the sugar sample, each division of rotation represents 1 per cent. of real sugar. The Laurent polarimeters made by Schmidt & Haensch of Berlin are provided with the Ventzke scale, for use with which 26·048 grammes is the standard quantity of sugar. Ventzke-divisions can be calculated into their equivalent in Soleil-divisions by multiplying by the factor 1·593. Sugar-units may be translated into circular degrees by multiplying the value of S for the light used by the rotation observed, and by twice the standard weight of sugar, and dividing the product by 10,000.

[2] The use of monochromatic light, *desirable* in saccharimetry, becomes absolutely *essential* for obtaining accurate polarimetric determinations of tartaric acid. This is due to the fact that Biot's law, that the angles of rotation for the different simple colours are proportional to the squares of the indices of refraction and inversely as the squares of the wave-lengths, is true of quartz and saccharine liquids, but does not hold good for tartaric acid solutions.

53. Another very ingenious and highly accurate method has been described by Broch. It consists in observing the spectrum of the polarised light after transmission through the optically active liquid. A spectroscope is employed, having a Nicol's prism behind the slit, and a similar prism as analyser, the solution-tube being placed between them in the usual manner. The light is then refracted by a prism, and then observed through a telescope in the usual way. A dark band appears on the spectrum owing to the complete absorption of the light of some particular wave-length. The position of the band depends on the rotatory power exerted by the solution, and it gradually shifts from one end of the spectrum to the other as the analyser is rotated. The observation is made by adjusting the vertical spider-line in the eye-piece of the telescope, so that it coincides in position with the Fraunhöfer line D, and the analyser is then rotated until the centre of the black band is coincident with the spider-line. The light used is either sun-light reflected from a heliostat, or a *luminous* gas or lamp-flame containing a bead of sodium chloride or carbonate.

54. Professor Jellett has devised a form of instrument in which the rotation produced by an active solution is neutralised by that of turpentine of the opposite kind. A rack-work arrangement allows the length of turpentine passed through to be varied as required, and the indications are read off on a scale. The instrument is fully described in Thudichum and Dupré's work on "Wine," and is stated to give very accurate results.

55. Before using the polarimeter the observing tube should be filled with distilled water and placed in position between the polarising and analysing prisms, which are then to be adjusted, so that the latter shall be at the zero point of the scale when there is no optical disturbance of the field. The tube is then filled with the solution to be tested and replaced between the polariser and analyser, when, if it contain an active substance, an optical disturbance will be observed, the extent and direction of which will depend on the amount and nature of the rotating substance under examination. The polarimeter is then adjusted, so that the neutral point is reached, or, in other words, so that the optical disturbance produced by the introduction of the rotating liquid is compensated, when the rotation required to produce this effect is read off and recorded. From the circular rotation observed, the specific rotatory power of the substance may be calculated in the manner described in the next paragraph.

Full directions for the preparation of the solution and the practical management of the polarimeter will be found in the section on the "Action of Sugars on Polarised Light."

SPECIFIC ROTATORY POWER.

56. The specific rotatory power of an optically active substance is the angular rotation exerted by it on a ray of polarised light which is caused to traverse a thickness of 1 decimetre (= 3·937 inches) of the pure substance.

57. The *absolute* specific rotatory power of a solid substance can only be observed if the body be obtainable in thick slices of considerable transparency. In default of these rarely attainable conditions, it is necessary to operate on a solution of known concentration, and from the *sensible* or *apparent* specific rotatory power observed, to calculate the *absolute* rotatory power of the solid substance.

58. The *sensible specific rotatory power* of an active body is often seriously affected by change of temperature or by the concentration of the solution. In some cases the rotation is increased and in others diminished by dilution, so that the value obtained for a given solution does not represent the absolute specific rotatory power of the pure substance, but differs from it to an unknown extent, which is dependent on the influence which may be exerted by the optically inactive solvent. The statement of the specific rotatory power of a body in solution is therefore of value only when the strength of the solution and the nature of the solvent are also given. Moreover, Oudemanns has shown that the influence of two solvents is often very different from that of either alone. Thus, a solution of cinchonine in absolute alcohol has a rotatory power of +228° for the D line, while the chloroform solution rotates +212° only. Yet a solution of equal strength in a mixture of 87 per cent. of chloroform and 13 per cent. of alcohol has a rotation of +237°.[1]

For various reasons the most accurate results are obtainable by working with highly concentrated solutions, and hence a liquid should be chosen which possesses a high power of solution for the optically active body.

The foregoing considerations have not hitherto received the consideration they deserve, to which circumstance is probably attributable the discordant statements on record as to the rotatory power of various optically active bodies.[2]

59. The sensible or apparent specific *rotatory power* of a substance is found by dividing the angular rotation

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[1] Tollens has found that solutions of cane sugar in methyl alcohol, ethyl alcohol, and acetone exhibit sensibly higher rotatory power than aqueous solutions of the same strength.—*Ber.* xiii. 2297.

[2] Further information on this interesting subject will be found in Watt's *Dictionary of Chemistry*, vol. viii. p. 1209 *et seq.*

observed in the polarimeter (a) by the length of the tube in decimetres (l), and by number of grammes in 1 c.c. of the liquid. This last figure is one-hundredth of the concentration (c), or grammes per 100 c.c. of the liquid. Thus, if S represent the specific rotatory power, then—

$$S = \frac{a}{l \times \frac{c}{100}} = \frac{100a}{l \times c}.$$

60. In all determinations of specific rotatory power it is necessary to take into account the refrangibility of the light employed for the observation. Formerly, an approximately monochromatic light was obtained by interposing a plate of deep red glass, the rotation observed being taken as that of "the red ray." The use of a bunsen flame in which a compound of sodium is heated, affords a strictly monochromatic light of the refrangibility of Fraunhofer's line D in the solar spectrum. When the corn-flower or transition tint is observed the results correspond closely, in the case of sugar solutions, with those obtained by observing the rotation of the "mean yellow ray." This is due to the *teinte du passage* being complementary to, and hence equally rotated with, the mean yellow ray. In consequence of the difference in the rotating action of circularly polarising liquids on rays of varying refrangibility, it is desirable always to state the nature of the light used. This is usually done by affixing a small letter as index to the number expressing the specific rotatory power of the substance. Thus $[a]_R$ is symbolical of the specific rotatory power for the mean red ray; $[a]_j$ for the mean yellow, or transition tint; and $[a]_D$ for the monochromatic light of incandescent sodium vapour. These symbols being somewhat clumsy, the author has suggested their replacement by the symbols S_R, S_j, and S_D.

Colour of Ray.	Angular Rotation.		
	Degrees.	Minutes.	Seconds.
Extreme red	17	29	47
Red glass (Cu_2O)	18	25	0
Limit of red and orange	20	28	47
,, orange and yellow	22	18	49
Mean yellow	24	0	0
Limit of yellow and green	25	40	31
,, green and blue	30	2	45
,, blue and indigo	34	34	18
,, indigo and violet	37	51	58
Extreme violet	44	4	58

61. The preceding table by Biot shows the rotation of rays of different refrangibilities produced by a plate of quartz 1 millimetre in thickness.

62. The following values have been found by Broch for the rotation produced by a thickness of 1 millimetre of quartz on light of the refrangibilities of the chief lines of the solar spectrum:—

B.	C.	D.	E.	F.	G.
15° 18′	17° 15′	21° 40′	27° 48′	32° 30′	42° 12′

Girard and De Luynes have recently determined with great care the deviation produced by a plate of quartz 1 millimetre in thickness, and find an angular rotation of 21° 48′ = 21°·8 for light of the refrangibility of the sodium line D, the possible error not exceeding 4′ = ·07°.

63. In the following table are given the apparent specific rotatory powers of some of the more important optically active organic substances. The letters refer to the refrangibility of the light employed, D signifying the sodium ray; and j (*jaune*) the mean yellow or transition tint. The relations of these values to each other in the case of quartz are indicated in the last paragraph, but they have different ratios in the case of other optically active substances:—

Table of Apparent Specific Rotatory Power of Organic Bodies.

Active Substance in Solution.	Formula.	Nature of Solvent.	Specific Rotatory Power.	
			D.	j.
Egg albumin . .	...	Water	−35·5	...
Serum albumin .	...	Water	−56·0	...
Coagulated albumin .	...	Potassa	−58·5	...
Casein . . .	...	Potassa	−91·0	...
Amygdalin . .	$C_{20}H_{27}NO_{11}$	Water	...	−35·5
Amylic alcohol. .	$C_5H_{12}O$	...	−4·38	...
Valeric acid . .	$C_5H_{10}O_2$	...	+4·2	...
Camphor . . .	$C_{10}H_{16}O$	Alcohol	±42·8	±47·4
Camphoric acid .	$C_{10}H_{16}O_4$	Water	...	±38·9
Terebenthene . .	$C_{10}H_{16}$	...	−40·3	...
Austra-terebenthene .	$C_{10}H_{16}$	...	+21·5	...
Iso-terebenthene .	$C_{20}H_{32}$	...	−10·5	...
Cholesterin . .	$C_{20}H_{44}O$	Alcohol	−31·6	...
Glycocholic acid .	$C_{26}H_{43}NO_6$	Alcohol	+29·0	...
Taurocholic acid .	$C_{26}H_{45}NSO_7$	Alcohol	...	+253
Tartaric acid . .	$C_4H_6O_6$	Water	...	±9·6
Tart. ammonium .	$C_4H_4O_6(NH_4)_2$	Water	...	±29·0
Malic acid . .	$C_4H_6O_5$	Water	...	−50·0
Santonin . . .	$C_{15}H_{18}O_3$	Alcohol	...	−230 at 20° C.

From this table the *carbohydrates* and *alkaloids* are omitted, as their rotatory action will be considered fully in other sections.

ULTIMATE or ELEMENTARY ANALYSIS.

64. When organic substances are heated to redness in the air or in presence of oxygen-yielding substances, they are generally completely oxidised, the carbon being burnt to carbon dioxide, and the hydrogen to water. Nitrogen is evolved for the most part in the free state, but in some cases partly in combination with oxygen. Sulphur and phosphorus are also converted into oxides, and the same is true of such of the metals as combine with oxygen at a red heat. A few substances, such as potassium cyanate, resist the action of dry air at a red heat. Substances containing the metals of the alkalies or alkaline earths in the form of salts of organic acids, leave these metals in the form of carbonates;[1] hence the carbon dioxide evolved in the form of gas will be less than that corresponding to the total carbon present.

65. Although an elementary analysis is frequently the most satisfactory mode of establishing the composition and even the identity of an organic substance, it is subject to grave disadvantages; for, as it merely determines the total amount of the elements present, it affords no clue to the arrangement of the atoms, and in many cases does not even give the number of atoms of each element present. Thus, the percentage of carbon and hydrogen in an organic substance having been duly determined, there would still be no indication which of the individual members of the particular group of bodies it might represent.

For example: suppose that a substance when analysed has been found to contain—

$$\begin{array}{l} C = 85{\cdot}74 \text{ per cent.} \\ H = 14{\cdot}28 \quad ,, \\ \hline \quad 100{\cdot}00 \end{array}$$

Dividing in each case the percentages of carbon and hydrogen by their respective atomic weights, we arrive at CH_2, as the simplest possible representation of the substance analysed. But this is the general expression for the large group of hydrocarbons called olefines, and the method is quite incompetent to tell us whether the substance examined really consisted of C_2H_4, ethylene; C_3H_6, propylene; C_4H_8, butylene; C_5H_{10}, amylene; or of any other member of the same homologous series expressed by the general formula C_nH_{2n}.

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[1] In a few instances other salts may be left. Thus, sodium sulphophenate leaves sodium sulphate on ignition.

Again, suppose the substance was found by analysis to have the following composition :—

$$\begin{aligned} C &= 40{\cdot}00 \text{ per cent.} \\ H &= 7{\cdot}27 \quad \text{,,} \\ O &= 52{\cdot}73 \quad \text{,,} \\ &\overline{100{\cdot}00} \end{aligned}$$

These figures correspond to the empirical formula CH_2O, or a multiple of this, and from the results of the elementary analysis *alone*, it might still be any one of the following bodies :—

$$C_nH_{2n}O_n = \begin{cases} CH_2O & = \text{Methylic aldehyde.} \\ C_2H_4O_2 & = \text{Ethylenic ether; acetic acid; methyl formate.} \\ C_3H_6O_3 & = \text{Lactic acid; paralactic acid; hydracrylic acid; methyl glycollate.} \\ C_6H_{12}O_6 & = \text{Dextrose; lævulose; \&c.} \end{cases}$$

66. Another serious difficulty which affects ultimate organic analysis is the necessity for extreme purity of the substance analysed, as a mixture of two bodies will give figures which baffle all attempts at interpretation. On the other hand, it might be supposed that the fact that an elementary analysis yielded figures closely in accordance with theory was in itself a guarantee of the purity of the body analysed. This, however, is by no means universally the case. In the first place, small proportions of foreign matter altogether escape detection, and in special cases as much as 10 per cent. or more of a common impurity will scarcely show itself in the percentages of carbon and hydrogen obtained. Thus the presence of 10 per cent. of common alcohol in ethyl acetate would cause a difference in the percentage of carbon of but 0·23 per cent., and in the hydrogen of 0·40 per cent. Similarly, 10 per cent. of amylic alcohol in amyl acetate would cause a variation of but 0·37 per cent. in the carbon, and 0·28 per cent. in the hydrogen.

Hence the value of elementary analysis as a means of chemically examining and assaying commercial organic products is comparatively limited, though for the purposes of original organic research it is simply irreplaceable. As this work is intended rather for use in the commercial laboratory than for employment by the student in search of new organic bodies, and as every text-book already published contains a description of the ordinary methods of making an organic combustion, it is unnecessary to give the details here, and to describe the methods at any length without working details would merely be waste of space.

The following general outlines may, however, be found of service in enabling a suitable method of analysis to be chosen.

67. **Carbon and Hydrogen** are determined by igniting the substance with dry oxide of copper, with or without the assistance of a stream of oxygen or purified air.[1] The resultant water is absorbed by sulphuric acid or dry calcium chloride, and the carbon dioxide by soda-lime or solution of caustic potash. In presence of sulphur, chlorine, bromine, iodine or light metals, chromate of lead is substituted for the cupric oxide.[2] Mercury is liable to distil over into the water-absorption apparatus. In presence of nitrogen the anterior part of the tube is filled with metallic copper. Silver may be substituted for the copper, and has the advantage that it retains chlorine and other haloid elements, but a very high temperature should be employed. W. H. Perkin recommends the use of potassium chromate, either granulated or absorbed by precipitated manganese dioxide. Oxides of sulphur are absorbed by this mixture (*Jour. Chem. Soc.*, xxxvii. 121, 457).

68. **Nitrogen** may be detected by heating the substance (if a liquid absorbed by asbestos or sand) with metallic sodium in a narrow test-tube. Cyanide is formed, and may be dissolved out with cold water. The filtered liquid should be treated with a drop each of ferrous sulphate and ferric chloride solutions, and then acidulated with hydrochloric acid, when a deep green coloration or Prussian-blue precipitate will indicate the formation of a cyanide.

69. Most organic compounds give off the whole of their contained nitrogen in the form of ammonia on ignition with soda-lime. If rich in nitrogen, an addition of sugar should be made to the soda-

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[1] F. Kopfer has described an apparently excellent method of organic analysis by burning the substance in oxygen, and passing the products of combustion over metallic platinum (*Jour. Chem. Soc.*, xxix. 660). Dupré has described a plan of determining very small quantities of carbon (*Jour. Chem. Soc.*, xxxv. p. 159.

[2] Schwartz and Pastrovich (*Chem. News*, xliii. 39) recommend, for the combustion of organic compounds of the light metals, an ingenious process based upon the ignition of the substance, mixed with excess of pure chromic oxide, in a current of oxygen. A chromate of the metal remains in the boat, the whole of the carbon being converted into carbon dioxide. The method appears capable of very general application.

lime, on each side of the substance to be analysed, so as to expel the air as completely as possible. Gruber has shown (*Jour. Chem. Soc.*, xl. 451) that the alleged inaccuracy of the soda-lime process for the generality of nitrogen estimations is without foundation, provided that proper precautions be observed.

70. Some nitrogenised bodies, such as indigo, yield volatile organic bases, instead of ammonia, on ignition with soda-lime. These all resemble ammonia in the fact that their hydrochlorides form double salts with platinic chloride, which on ignition leave 194·87 parts of Pt for 28 of N.

71. *Nitro-substitution compounds*, such as picric acid, do not evolve the whole of their contained nitrogen in the form of ammonia when ignited with soda-lime. Addition of sugar improves the result.[1]

72. *Cyanogen compounds* may be analysed by ignition with soda-lime, if a high temperature be ultimately employed. The use of sugar is desirable.

73. *A general process* for the determination of nitrogen in organic bodies consists in combustion with oxide of copper, passing the gaseous products over red-hot metallic copper or silver, absorption of the carbon dioxide and water by solution of potash, and measurement of the residual gaseous nitrogen. An improved apparatus for collecting and measuring the nitrogen, and method of conducting the combustion generally, has been described by C. E. Groves (*Jour. Chem. Soc.*, xxxvii. 500). Gruber, Johnson and Jenkins (*Chem. News*, xlvii. 146; l. 191), and others have proposed modifications of Dumas' general process. V. Meyer has found that in the case of nitrogenous bodies containing much sulphur it is necessary to replace the oxide of copper by a thick layer of lead chromate, and to conduct the combustion very slowly. The nitrogen obtained should be tested for carbon monoxide (*Jour. Soc. Chem. Ind.*, iii. 455).

74. **Chlorine, Bromine, and Iodine** may be detected

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[1] J. Ruffle (*Jour. Chem. Soc.*, xxxix. 87) recommends the addition of sodium thiosulphate to the soda-lime when the nitrogen of nitro-compounds is to be determined. His results are very satisfactory. A. Guyard (*Chem. News*, xlv. 159) recommends the addition of sodium acetate, and claims that by this means the whole of the contained nitrogen, in whatever form it existed, is obtained as ammonia. C. Arnold, however, finds neither Ruffle's nor Guyard's method to be wholly satisfactory. His best results were obtained by a combination of the two, in which the substance was burnt with a mixture of equal parts of anhydrous sodium acetate, sodium thiosulphate, and soda-lime (*Repert. Anal. Chem.*, 1882, p. 21). For the method adopted by the German Manure Manufacturers' Association for determining the nitrogen in manures, see the *Chemical News*, l. 180.

by igniting the substance in a stream of hydrogen, and passing the gas into nitrate of silver. They may be determined by ignition with excess of pure quicklime and pounded glass, with subsequent conversion into silver salts. Mulder and Hamburger prepare the quicklime by igniting precipitated calcium carbonate in a stream of pure hydrogen. In some cases (*e.g.* the analysis of benzene hexa-chloride) ignition with lime alone does not give correct results, but by using a mixture of lime and potassium nitrate all the chloride is obtained in a form precipitable by silver solution. Another good method is based on ignition of the substance with ferric oxide, with subsequent conversion to silver salts (Kopp., *Deut. Chem. Ges. Ber.*, viii. 769, and Klobukowski, x. 290.) Carius heats the substance to be analysed in a sealed tube, with fuming nitric acid and silver nitrate. The method gives good results, but the risk attending the bursting of the tube, the uncertain period during which the tube must be heated to ensure complete decomposition, and the semi-molten condition in which the precipitate is often obtained, are objections to the process.

75. Plimpton and Groves (*Jour. Chem. Soc.*, xlii. 120) determine the halogens in volatile organic bodies by burning the substance gradually in a bunsen flame, placed under a trumpet-shaped tube, and absorb the products of combustion in solution of caustic soda, which is subsequently acidulated with nitric acid and precipitated by nitrate of silver. The test analyses by this method are highly satisfactory, and the process is rapid and simple.

76. **Sulphur, Phosphorus, and Arsenic**[1] may be detected by igniting the substance with pure soda-lime mixed with an oxidising agent, such as nitre, chlorate of potassium, or mercuric oxide. The residue is tested for sulphates, phosphates, and arseniates. The process may be made quantitative. Another method is to heat the substance in a sealed tube with nitric acid of 1·2 sp. gr. The sulphur, phosphorus, and arsenic are converted respectively into sulphuric, phosphoric, and arsenic acids.

Sulphur and the halogens may also be detected by heating the substance with sodium, which converts them into sulphide, chloride, &c., capable of ready recognition.

77. **Metals** usually remain in the residue obtained on igniting the organic substance in the air. Metals of the alkalies and alkaline earths are usually left as carbonates, but sometimes more or less completely as sulphates, phosphates, chlorides, &c. Heavy metals

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[1] A comprehensive and apparently accurate method for determining these elements has been described by Brügelmann (*Zeits. Anal. Chem.*, xvi. 1, and *Jour. Chem. Soc.*, xxxi. 739).

are usually left as oxides, except silver, gold, and platinum, which will remain in the free state. Arsenic, antimony, and other metals, when existing in volatile compounds, may be completely volatilised.

78. *Mercury* will be wholly volatilised. It may be determined in all instances by igniting the substance with soda-lime, and collecting and weighing the mercury which distils over.

79. **Oxygen** may be detected in organic bodies containing it by ignition in a stream of hydrogen, when water will be formed. By igniting the substance in a stream of chlorine, or in admixture with potassium chloroplatinate, carbon dioxide will be formed if oxygen be present. Hydrochloric acid and chlorine may be respectively absorbed by solutions of lead nitrate and stannous chloride, and the carbonic acid passed into baryta water or potash solution. In the great majority of cases the oxygen of organic bodies is *determined* "by difference."

BEHAVIOUR OF ORGANIC BODIES WITH SOLVENTS.

80. In the proximate analysis of plants and other complex substances of organic origin, a systematic treatment with solvents is a most valuable means of separating different classes of bodies from each other. The systematic use of solvents has been worked out very thoroughly by Dragendorff and others, whose methods will be described in greater detail in future sections. In proximate organic analysis only a limited use is made of the stronger acids so largely employed in mineral analysis, while the use of alcohol, ether, chloroform, and other physical solvents is greatly extended.

81. **Exhaustion of Organised Tissues by Solvents.**—In assaying commercial organic substances it is often requisite to effect as perfect an exhaustion as possible of an organised tissue of some active principle or valuable constituent existent therein. This is the case in the assay of cinchona barks for alkaloid, of seeds and oil-cakes for oil, and of sugar-cane and beetroot for sugar. In such cases the cells which contain the principles to be extracted are only incompletely ruptured by the most careful pounding or crushing of the sample, and hence solvents can only act on the contents through the cell walls, and the resultant solution can only pass through the cell walls by diffusion. This often renders the process of exhausting organised tissues very

tedious, while the difficulty is enhanced by the fact that economy and convenience of subsequent treatment often render it desirable or necessary to use a very limited quantity of solvent. Under these circumstances, an apparatus which will act almost automatically, and allow of complete exhaustion by a small quantity of solvent, possesses great advantages.

82. **Soxhlet's Tube.**—For the automatic exhaustion of a substance by a volatile solvent, no better arrangement has been described than an ingenious device of Soxhlet's (fig 5). The substance to be extracted is enclosed in a plaited filter or cylinder of filter paper, or if it be coarse it is sufficient simply to place it loose in a large test-tube, having an aperture at the bottom closed by a plug of glass-wool. Thus arranged, the tube or filter with its contents is placed in a Soxhlet tube, having a little glass-wool at the bottom, and adapted by means of a cork to a flask containing the solvent. A vertical condenser (fig. 6) is adapted to the upper end of the Soxhlet's tube, and the solvent kept boiling by a suitable source of heat. In the case of petroleum spirit, ether, or other volatile and inflammable solvent, this should be a tin vessel of water kept hot by a small flame. As the solvent boils it is condensed and falls on the substance to be extracted, remaining in contact with it until both the inner and outer tubes are filled to the level of the syphon, when the solution passes off into the flask, to be redistilled and recondensed, and so on until the process is judged to be complete. With a proper arrangement of the source of heat, the extraction goes on regularly and automatically. On changing the flask and replacing the inner tube by one containing a fresh sample, the apparatus is ready to be used for another extraction.

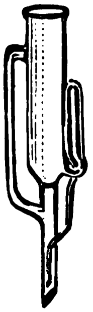

Fig. 5.

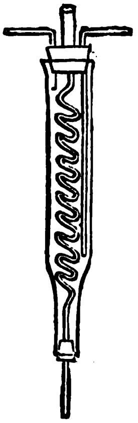

Fig. 6.

83. A very simple and convenient form of exhauster, adapted either for extraction or repercolation, has been described by Dunstan & Short (*Pharm. Jour.*, [3] xiii. 664). It consists of two glass tubes, the wider of which is drawn out at one end. The narrower and somewhat shorter tube fits into the outer one with much margin, and is also drawn out in such a way as to allow the end to protrude from the drawn-out end of the wider tube when the smaller is inserted therein. At the point where the outer tube commences to contract it is indented on opposite sides, by which means two ledges are formed within the tube which serve as

supports for the narrower tube.[1] The inner tube serves to contain the substance to be exhausted. The lower drawn-out end of the wider tube is fitted by a cork to the flask containing the volatile solvent, while the upper end is connected with a condensing arrangement.

84. J. West-Knights has described a form of exhauster which may be conveniently used when the quantity of material to be extracted is somewhat small (*Analyst*, viii. 65). A percolator is made by cutting off the bottom from a test-tube of suitable size, and blowing a hole in the side of the tube about an inch from the top. A disc of filter paper or fine cambric is tied over the lower end of the tube. The substance to be extracted is placed in the tube, and kept in its place by some glass-wool and a perforated disc of metal, and the tube with its contents then fixed by a cork to the lower end of the tube of a vertical condenser. This is adapted by a larger cork to the neck of an ordinary flask containing the volatile solvent, on heating which the vapour passes through the hole in the side of the test-tube up into the tube of the condenser, where it is liquefied. The condensed liquid drops right into the test-tube, percolates through the substance to be extracted, and falls to the bottom of the flask, to be again volatilised. As the percolator is inside the flask, its contents are kept constantly at the boiling point of the solvent, and, the action being continuous and automatic, very rapid exhaustion may be effected.

Other forms of exhauster have been contrived by Church, Drechsel, Angell, Thoms, Thresh (*Pharm. Jour.*, [3] xv. 281) and others, but those already described will be found sufficient for all purposes.

85. **Employment of Immiscible Solvents.**—In mineral analysis this method finds but few applications, but in proximate organic analysis, one of the most valuable means of effecting separations consists in agitating the solution of a substance in one solvent, with another solvent insoluble or only slightly soluble in the former liquid. Under these circumstances, the dissolved body is distributed between the two solvents in proportions which are probably dependent on the relative solubility of the substance in the two media, and the relative quantities of the two media employed. Thus, it may be supposed, that, if a substance be 99 times more soluble in chloroform than in water, and its aqueous solution be shaken with an equal measure of chloroform, 99 per cent. of the whole substance will pass into the

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[1] The indentations are made by gently pressing each side of the tube when red-hot with a pair of crucible tongs.

chloroform. On separating this layer, and again agitating the residual aqueous liquid with an equal quantity of chloroform, 99 per cent. of the remaining substance will be dissolved, thus making the exhaustion practically complete. Something also depends on the quantity of solvent employed, and the temperature at which the operation is conducted.

86. In making a proximate analysis by means of immiscible solvents, much of the success in practice depends on the care and skill with which the manipulation is conducted. The most convenient apparatus for effecting the treatment consists of a pear-shaped (fig. 7) or cylindrical (fig. 8) glass separator, furnished with a tap below and a stopper at the top. The tube below the tap should be ground obliquely so as to prevent loss of liquid by imperfect delivery. Supposing that it be desired to effect the separation of a substance from an aqueous liquid by agitation with ether, the former is introduced into the separator, of which it should not occupy more than one-third, acid or alkali added as may be desired, and next a volume of ether about equal to that of the aqueous liquid. The stopper is then inserted and the whole thoroughly shaken together for a minute or two, and then set aside. As a rule, the contents will readily separate into two well-defined layers, the lower of which is aqueous and the upper ethereal. Sometimes separation into layers does not occur readily, the liquid remaining apparently homogeneous, forming an emulsion or assuming a gelatinous consistency. In such cases, separation may sometimes be induced by thoroughly cooling the contents of the separator. In the case of ether, the separation may always be effected by adding an additional quantity of ether and reagitating, or, when the employment of a sufficient excess of ether is inconvenient or impracticable, the addition of a few drops of alcohol, followed by a gentle rotatory motion of the liquid, will almost invariably cause separation to occur promptly.

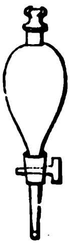

Fig. 7.

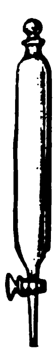

Fig. 8.

87. Separation having taken place, the aqueous layer should be run off by the tap into another separator, where it can again be agitated with ether to insure the complete removal of the body to be dissolved therein. The ethereal liquid remaining in the first separator should be shaken with a fresh quantity of alkalised or acidulated water, which is then tapped off as before, and the remaining traces removed by treating the ether with a little pure water. This having in turn been run off to the last drop, the ethereal solution can next be removed by the tap, but a preferable

plan is to pour it out of the top of the separator, by which means any contamination by the traces of water adhering to the sides of the glass will be avoided.

88. When amylic alcohol, benzene, or petroleum ether is employed, the manipulation is the same as that just described; but when chloroform is used, or a mixture containing a considerable proportion of that solvent, the aqueous liquid forms the upper stratum, and the chloroformic solution can at once be removed by the tap.

89. The tendency to form an obstinate emulsion is greater when the aqueous liquid is alkaline, and is often very troublesome when chloroform, benzene, or petroleum ether is substituted for ether. In such cases, the employment of a larger quantity of the solvent sometimes causes separation, but, when admissible, a better plan is the addition of ether. This answers very successfully for the isolation of strychnine, which is nearly insoluble in unmixed ether but readily soluble in a mixture of equal measures of ether and chloroform. This solvent is heavier than water, and is capable of very extensive application.

It is evident that the treatment can be repeated any number of times requisite to ensure the complete extraction of substances having a limited solubility in the solvents employed, and these can themselves be varied in a systematic matter, as is done in Dragendorff's method for the separation of alkaloids and other active principles.

90. The following table (91) shows the behaviour of the principal organic substances on treatment with acidulated and alkalised water, and solvents immiscible therewith, such as ether, chloroform, amylic alcohol, benzene, and petroleum ether. It must not, however, be supposed that the immiscible solvents can be employed indifferently, as some of the bodies are removed from their aqueous solutions by one solvent, but are unaffected by others owing to their limited solubility therein. This is especially the case with the alkaloids and glucosides, and hence the table must merely be regarded as showing their general tendency, their behaviour when treated with the individual solvents being deferred for full description later on. With regard to the remaining compounds, the choice of solvents will be simplified by a study of the second table (92) which gives the solubilities of a large number of them. Carbohydrates and proteids are omitted as being generally insoluble in liquids immiscible with water, and the statement of solubilities of the alkaloids or glucosides is deferred. The sign ∞ signifies that the substance and solvent are miscible in all proportions.

91. Table showing the Behaviour of Organic Substances with Immiscible Solvents.

On *agitating the substance with water, acidulated with sulphuric acid, and a suitable solvent immiscible therewith (such as ether, chloroform, amylic alcohol, benzene, or petroleum ether), the following distribution will occur*:—

The Acidulated Aqueous Liquid will contain *carbohydrates, soluble alkaloids and acids, organic bases, proteids*, &c., which may be further separated by adding a moderate excess of soda, and again shaking with a suitable immiscible solvent, when there will be obtained:—		The Immiscible Layer will contain *hydrocarbons, oils, various acids, resins, colouring matters, phenols, glucosides*, &c., which may be further separated by agitating the liquid with water containing caustic soda, when there will be obtained:—	
In the Alkaline Aqueous Liquid— *Carbohydrates*; as sugars, gums, dextrin. *Soluble Alcohols*; as methyl alcohol, ethyl alcohol, glycerin. *Soluble Acids*; as acetic, oxalic, lactic, malic, tartaric, sulphophenic. *Certain Alkaloids or Organic Bases*; as curarine, urea, glycocine, solanine, and possibly cinchonine, morphine, and pyridine. *Certain colouring matters*; as indigo products. *Proteids and their allies*; as albumin, casein, gelatin.	In the Immiscible Layer— *Most Vegetable Alkaloids*; as quinine, strychnine, aconitine, atropine, nicotine (cinchonine, morphine, the last two with difficulty). *Coal Tar Bases*; as aniline and its homologues, (rosaniline), chrysotoluidine, (pyridine), homologues of pyridine.	In the Alkaline Aqueous Liquid— *Fatty Acids*; as stearic, oleic, valeric. *Various other Acids*; as benzoic, salicylic, phthalic, meconic. *Acid Dyes and Colouring Matters*; as picric and chrysophanic acids, alizarin, aurin, bilirubin. *Acid Resins*; as colophony. *Phenols*; as carbolic and cresylic acids, thymol, creasote. *Certain Glucosides, &c.*; as santonin, cantharidin, picrotoxin.	In the Immiscible Layer— *Solid Hydrocarbons*; as paraffin, naphthalene, anthracene. *Liquid Hydrocarbons*; as petroleum products, rosin-oil, benzene. *Essential Oils*; as turpentine. *Nitro-compounds*; as nitro-benzene. *Ethers and their Allies*; as ether, chloroform, compound ethers, nitro-glycerine. *Fixed Oils, Fats, and Waxes.* *Neutral Resins and Colouring matters.* *Camphors*; as laurel-camphor, borneol, menthol. *Alcohols* insoluble or nearly insoluble in water; as amyl and cetyl alcohols, cholesterin. *Certain Glucosides, &c.*; as saponin, digitalin, santonin. *Certain Weak Alkaloids*; as caffeine, colchicine, narcotine, piperine, theobromine.

92. Table showing the Behaviour of various Organic Substances with Solvents.

Name of Substance.	Formula.	Solubility in 100 parts of										Remarks.
		Cold Water.	Boiling Water.	10 per cent. NaHO solution.	Rectified Spirit.	Amylic Alcohol.	Ether.	Chloroform.	Carbon Disulphide.	Benzene.	Petroleum Ether.	
Ethyl alcohol	C_2H_6O	∞	∞	∞	∞	∞	∞	∞	S	∞	∞	Any contained water is separated by excess of 5 last solvents.
Amyl alcohol	$C_5H_{12}O$	2½	...	2½	∞	∞	∞	∞	∞	∞	∞	Soluble in acetic acid mixed with equal volume of water.
Glycerin	$C_3H_8O_3$	∞	∞	∞	∞	...	I	I	I	I	I	
Nitro-glycerin	$C_3H_5N_3O_9$	I	I	I	S	...	S	...	...	...	...	Decomposed by boiling soda solution. Soluble in wood spirit.
Ether	$C_4H_{10}O$	10	...	10	∞	∞	∞	∞	∞	∞	∞	
Chloral hydrate	C_2HCl_3O, H_2O	67	S	(S)	S	...	S	S	S	S	S	Decomposed by soda with separation of chloroform.
Chloroform	$CHCl_3$	I	I	I	S	∞	∞	∞	∞	∞	∞	
Iodoform	CHI_3	I	I	I	1¼	...	S	S	S	(S)	(S)	Dissolved by 13,000 parts of cold water.
Acetic acid	$C_2H_4O_2$	∞	∞	∞	∞	∞	(S)	...	...	...	...	Soluble in ether only when anhydrous.
Oxalic acid (crystallised)	$C_2H_2O_4, 2H_2O$	8	350	S	15	...	(I)	I	...	I	I	Soluble in ether to extent of 1¼%.
Lactic acid	$C_3H_6O_3$	∞	∞	S	∞	S	∞	(S)	...	...	...	
Succinic acid	$C_4H_6O_4$	8	60	S	12½	...	15	I	...	I	...	Soluble in 13 parts of absolute alcohol. Decomposed on boiling.
Tartaric acid	$C_4H_6O_6$	25	100	S	41	...	(I)	I	...	I	I	Soluble in ether to extent of ·4%. Decomposed by fusion.
Citric acid	$C_6H_8O_7, H_2O$	133	200	S	53	...	2¼	I	...	I	I	Absolute alcohol dissolves 39%.
Meconic acid	$C_7H_4O_7, 3H_2O$	·9	S	S	12	...	I	...	...	...	...	Soluble in about 150 parts of ether.
Gallic acid	$C_7H_6O_5, H_2O$	I	33	S	23	...	2½	...	...	...	...	Decomposed by heat. Very soluble in absolute alcohol.
Pyrogallic acid	$C_6H_6O_3$	33	S	S	S	...	S	I	...	...	...	Solution in soda turns rapidly brown in air.
Gallo-tannic acid	Indefinite	S	S	S	S	...	(I)	I	I	I	I	Soluble in acetic ether.

Name of Substance.	Formula.	Cold Water.	Boiling Water.	10 per cent. NaHO Solution.	Rectified Spirit.	Amylic Alcohol.	Ether.	Chloroform.	Carbon Disulphide.	Benzene.	Petroleum Ether.	Remarks.
Sulphophenic acid	$C_6H_6SO_4$	S	S	S	S	...	I	I	...	...	...	Decomposed on boiling.
Picric acid	$C_6H_3N_3O_7$	1	S	S	S	S	S	S	S	S	S	
Benzoic acid	$C_7H_6O_2$	⅓	8	S	42	...	31	S	S	S	S	
Salicylic acid	$C_7H_6O_3$	(I)	S	S	42	...	50	...	...	S	...	
Phthalic acid	$C_8H_6O_4$	⅛	S	S	S	...	S	...	...	S	...	Very slightly soluble in cold water.
Chrysophanic acid	$C_{15}H_{10}O_4$	I	(I)	S	S	...	S	S	...	S	S	
Hippuric acid	$C_9H_9NO_3$	¼	S	S	S	...	I	I	...	I	...	Alkaline solution is purple-red.
Uric acid	$C_5H_4N_4O_3$	I	I	S	I	...	I	...	...	...	...	
Higher fatty acids	Various	I	I	S	S	S	S	S	S	S	S	Aqueous and alkali solutions precipitated by excess of soda.
Fixed oils	Various	I	I	I	(I)	S	S	S	S	S	S	Castor oil is soluble in spirit and insoluble in petroleum ether.
Oil of turpentine	$C_{10}H_{16}$	I	I	I	∞	S	∞	∞	∞	∞	∞	
Camphor	$C_{10}H_{16}O$	I	I	I	S	...	S	S	S	...	...	
Paraffin wax	C_nH_{2n+2}	I	I	I	(I)	...	S	S	S	S	S	Soluble in hot absolute alcohol, insoluble in cold.
Benzene	C_6H_6	I	I	I	∞	S	∞	∞	S	∞	∞	
Nitro-benzene	$C_6H_5NO_2$	I	I	I	∞	...	∞	...	...	∞	...	
Naphthalene	$C_{10}H_8$	I	I	I	S	...	S	S	S	S	S	
Anthracene	$C_{14}H_{10}$	I	I	I	(S)	...	S	S	S	S	(I)	Sparingly soluble in cold spirit, ether, or benzene.
Alizarin	$C_{14}H_8O_4$	I	(I)	S	S	...	S	...	S	S	...	Slightly soluble in hot water.
Aurin	$C_{19}H_{14}O_3$	I	I	S	S	...	S	I	I	I	S	Slightly soluble in water. Alkaline solutions red.
Indigotin	$C_{16}H_{10}N_2O_4$	I	I	I	I	S	I	S	S	I	...	Soluble in hot aniline, phenol, and creasote, and in strong sulphuric acid.
Carbolic acid (absolute)	C_6H_6O	8⅓	S	S	∞	...	∞	∞	∞	∞	S	Sparingly soluble in cold petroleum spirit.
Resorcinol	$C_6H_6O_2$	S	S	S	S	...	S	I	I	(S)	...	Soluble in hot benzene; deposited on cooling.
Orcinol	$C_7H_8O_2+H_2O$	S	(S)	...	S	...	S	...	...	S	...	Soluble with difficulty in hot water and in alkaline solutions.
Thymol	$C_{10}H_{14}O$	(I)	...	S	100	...	S	...	...	...	...	Insoluble in small quantities of soda. Soluble in 1000 of water.
Menthol	$C_{10}H_{20}O$	I	I	I	S	...	S	...	...	S	...	
Creasote (mixture)	$C_8H_{10}O_2$; &c.	...	I	(S)	S	...	∞	∞	∞	∞	∞	Soluble with difficulty in soda. Insoluble in ammonia.

92. Table showing the Behaviour of various Organic Substances with Solvents.

Name of Substance.	Formula.	Solubility in 100 parts of										Remarks.
		Cold Water.	Boiling Water.	10 per cent. NaHO solution.	Rectified Spirit.	Amylic Alcohol.	Ether.	Chloroform.	Carbon Disulphide.	Benzene.	Petroleum Ether.	
Ethyl alcohol	C_2H_6O	∞	∞	∞	∞	∞	∞	∞	S	∞	∞	Any contained water is separated by excess of 5 last solvents.
Amyl alcohol	$C_5H_{12}O$	2½	...	2½	∞	∞	∞	∞	∞	∞	∞	Soluble in acetic acid mixed with equal volume of water.
Glycerin	$C_3H_8O_3$	∞	∞	∞	∞	...	I	I	I	I	I	
Nitro-glycerin	$C_3H_5N_3O_9$	I	I	I	S	...	S	...	...	...	...	Decomposed by boiling soda solution. Soluble in wood spirit.
Ether	$C_4H_{10}O$	10	...	10	∞	∞	∞	∞	∞	∞	∞	
Chloral hydrate	C_2HCl_3O, H_2O	67	S	(S)	S	...	S	S	S	S	S	Decomposed by soda with separation of chloroform.
Chloroform	$CHCl_3$	I	I	I	S	∞	∞	∞	∞	∞	∞	
Iodoform	CHI_3	I	I	I	1¼	...	S	S	S	(S)	(S)	Dissolved by 13,000 parts of cold water.
Acetic acid	$C_2H_4O_2$	∞	∞	∞	∞	∞	(S)	...	...	...	...	Soluble in ether only when anhydrous.
Oxalic acid (crystallised)	$C_2H_2O_4, 2H_2O$	8	350	S	15	...	(I)	I	...	I	I	Soluble in ether to extent of 1¼%.
Lactic acid	$C_3H_6O_3$	∞	∞	S	∞	S	∞	(S)	...	...	...	
Succinic acid	$C_4H_6O_4$	8	60	S	12½	...	15	I	...	I	...	Soluble in 13 parts of absolute alcohol. Decomposed on boiling.
Tartaric acid	$C_4H_6O_6$	25	100	S	41	...	(I)	I	...	I	I	Soluble in ether to extent of ·4%. Decomposed by fusion.
Citric acid	$C_6H_8O_7, H_2O$	133	200	S	53	...	2¼	I	...	I	I	Absolute alcohol dissolves 39%.
Meconic acid	$C_7H_4O_7, 3H_2O$	·9	S	S	12	...	I	...	...	...	...	Soluble in about 150 parts of ether.
Gallic acid	$C_7H_6O_5, H_2O$	I	33	S	23	...	2½	...	...	...	...	Decomposed by heat. Very soluble in absolute alcohol.
Pyrogallic acid	$C_6H_6O_3$	33	S	S	S	...	S	I	...	...	...	Solution in soda turns rapidly brown in air.
Gallo-tannic acid	Indefinite	S	S	S	S	...	(I)	I	I	I	I	Soluble in acetic ether.

NAME OF SUBSTANCE.	Formula.	Solubility in 100 parts of										REMARKS.
		Cold Water.	Boiling Water.	10 per cent. NaHO Solution.	Rectified Spirit.	Amylic Alcohol.	Ether.	Chloroform.	Carbon Disulphide.	Benzene.	Petroleum Ether.	
Sulphophenic acid	$C_6H_6SO_4$	S	S	S	S	...	I	I	...	...	...	Decomposed on boiling.
Picric acid	$C_6H_3N_3O_7$	1	S	S	S	S	S	S	S	S	S	
Benzoic acid	$C_7H_6O_2$	$\frac{1}{3}$	8	S	42	...	31	S	S	S	S	
Salicylic acid	$C_7H_6O_3$	(I)	S	S	42	...	50	...	...	S	...	Very slightly soluble in cold water.
Phthalic acid	$C_8H_6O_4$	$\frac{1}{6}$	S	S	S	...	S	...	...	S	...	
Chrysophanic acid	$C_{15}H_{10}O_4$	I	(I)	S	S	...	S	S	...	S	S	Alkaline solution is purple-red.
Hippuric acid	$C_9H_9NO_3$	$\frac{1}{4}$	S	S	S	...	I	I	...	I	...	
Uric acid	$C_5H_4N_4O_3$	I	I	S	I	...	I	...	...	...	...	
Higher fatty acids	Various	I	I	S	S	S	S	S	S	S	S	Aqueous and alkali solutions precipitated by excess of soda.
Fixed oils	Various	I	I	I	(I)	S	S	S	S	S	S	Castor oil is soluble in spirit and insoluble in petroleum ether.
Oil of turpentine	$C_{10}H_{16}$	I	I	I	∞	S	∞	∞	∞	∞	∞	
Camphor	$C_{10}H_{16}O$	I	I	I	S	...	S	S	S	...	...	
Paraffin wax	C_nH_{2n+2}	I	I	I	(I)	...	S	S	S	S	S	Soluble in hot absolute alcohol, insoluble in cold.
Benzene	C_6H_6	I	I	I	∞	S	∞	∞	S	∞	∞	
Nitro-benzene	$C_6H_5NO_2$	I	I	I	∞	...	∞	...	...	∞	...	
Naphthalene	$C_{10}H_8$	I	I	I	S	...	S	S	S	S	S	Sparingly soluble in cold spirit, ether, or benzene.
Anthracene	$C_{14}H_{10}$	I	I	I	(S)	...	S	S	S	S	(I)	
Alizarin	$C_{14}H_8O_4$	I	(I)	S	S	...	S	...	S	S	...	Slightly soluble in hot water.
Aurin	$C_{19}H_{14}O_3$	I	I	S	S	...	S	I	I	I	S	Slightly soluble in water. Alkaline solutions red.
Indigotin	$C_{16}H_{10}N_2O_4$	I	I	I	I	S	I	S	S	I	...	Soluble in hot aniline, phenol, and creasote, and in strong sulphuric acid.
Carbolic acid (absolute)	C_6H_6O	8½	S	S	∞	...	∞	∞	∞	∞	S	Sparingly soluble in cold petroleum spirit.
Resorcinol	$C_6H_6O_2$	S	S	S	S	...	S	I	I	(S)	...	Soluble in hot benzene; deposited on cooling.
Orcinol	$C_7H_8O_2+H_2O$	S	(S)	...	S	...	S	...	...	S	...	Soluble with difficulty in hot water and in alkaline solutions.
Thymol	$C_{10}H_{14}O$	(I)	...	S	100	...	S	...	...	...	...	Insoluble in small quantities of soda. Soluble in 1000 of water.
Menthol	$C_{10}H_{20}O$	I	I	I	S	...	S	...	...	S	...	
Creasote (mixture)	$C_8H_{10}O_2$; &c.	...	I	(S)	S	...	∞	∞	∞	∞	∞	Soluble with difficulty in soda. Insoluble in ammonia.

BEHAVIOUR OF ORGANIC BODIES WITH REAGENTS.

93. The action of chemical reagents on organic substances is of too diverse a nature to admit of generalisation, and the methods of experiment too well known to require special description. Treatment with reagents not only results in the formation of definite compounds, but in the production of various new bodies by the decomposition of the original substances, many of these decomposition products having more characteristic properties than the bodies from which they were derived.

94. **Normal Solutions.**—In describing standard solutions for volumetric determinations, the terms "normal," "decinormal," &c., are employed in this work in the same signification in which they are used by Sutton.[1] Thus, a normal solution is one containing, in 1000 cubic centimetres (= 1 litre), such an amount of the active constituent as will combine with, replace, or oxidise 1 gramme of hydrogen. Hence normal and decinormal solutions of the following substances have the strengths given below :—

				Grammes per litre.
Normal caustic soda	contains	Na	=	23
,, ,, ,,	,,	NaHO	=	40
,, ,, potash	,,	KHO	=	56·1
,, carbonate of sodium	,,	$\frac{Na_2CO_3}{2}$	=	53
Decinormal lime water	,,	$\frac{CaO}{20}$	=	2·8
,, baryta water	,,	$\frac{BaO}{20}$	=	7·65
Normal hydrochloric acid	,,	HCl	=	36·5
,, sulphuric acid	,,	$\frac{H_2SO_4}{2}$	=	49
,, oxalic acid	,,	$\frac{H_2C_2O_4, 2H_2O}{2}$	=	63
Decinormal silver nitrate	,,	$\frac{AgNO_3}{10}$	=	17·0
,, mercuric chloride	,,	$\frac{HgCl_2}{20}$	=	13·55
,, potassium permanganate	,,	$\frac{KMnO_4}{50}$	=	3·162

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[1] A use of the term "normal" has been made by Pattison Muir, Hannay, and others, which is apt to cause much misunderstanding. Pattison Muir calls a sulphuric acid "normal" which contains 98 grammes of H_2SO_4 per litre, so that his "normal sulphuric acid" has twice the neutralising power of the "normal hydrochloric acid" containing 36·5 HCl per litre. Similarly his normal sodium carbonate has twice the alkalinity of his normal caustic soda.

EXAMINATION FOR INORGANIC MATTERS.

95. The method of detecting and estimating the mineral constituents of an organic substance usually consists simply in igniting a known weight of the body in free contact with the air, and weighing the residue or *ash*.

The most satisfactory method of determining the *ash* of organic bodies is to conduct the ignition in a platinum tray or flat capsule placed in a gas-muffle maintained at the lowest temperature compatible with combustion. The tray should be supported on a row of pieces of tobacco-pipe stems or other non-conducting substance, so as to avoid over-heating from contact with the bottom of the muffle. If a bunsen burner be employed to effect combustion, similar care should be taken to avoid over-heating. If too high a temperature be employed there is great danger of loss by volatilisation of chlorides or carbonates of the alkali metals, and additional trouble may arise from fusion of the remaining ash, with consequent enclosure of particles of unburnt carbon. By keeping the temperature as low as possible, and avoiding local heating, nearly all organic substances can be burnt completely and without difficulty. In obstinate cases, the unconsumed matter may be mixed with nitrate of ammonium, or moistened with a strong solution of the salt, and then re-ignited. Addition of pure mercuric oxide is also useful occasionally, or the refractory matter may be mixed with a known weight of dry ferric oxide and again ignited.

96. In very many instances the difficulty of effecting complete combustion, and the danger of loss by volatilisation, may be wholly overcome by moistening the substance to be ignited, or the carbonaceous residue therefrom, with strong sulphuric acid. This converts the readily fusible and volatile chlorides and carbonates into the more fixed *sulphates* of the alkali metals, and on ignition complete combustion will readily ensue. It is desirable to moisten the ash with a drop of sulphuric acid and re-ignite, so as to get rid of any sulphides left after the first ignition. For the estimation of the ash of animal matters, it is desirable to treat the substance in a porcelain crucible with a mixture of strong nitric and sulphuric acids. This dissolves and destroys the organic matters before ignition, and, on evaporating the liquid to dryness and igniting the residue, complete combustion ensues, and a white "sulphated ash" is readily obtained. The same modification of the usual method of determining the ash of plants may be pursued with advantage in many cases, the starch and cellulose being first converted into oxalic acid, which the sulphuric acid decomposes into oxides of carbon and water, so that after evaporation of the acid there is but little organic mattter left to ignite.

97. Sulphuric acid is almost always employed in determining the ash of commercial sugars, a deduction being made from the weight obtained for the increase due to "sulphation."

98. Besides being in excess of the true ash, the "sulphated ash" will contain no chlorides or carbonates. Phosphoric and silicic acids are not affected by the treatment.

99. It must be remembered, however, that the *carbonate* present in the ash left on igniting organic bodies, is really the *skeleton of the salts of organic acids* present in the original substance. Hence, many plant analysts deduct the carbonic acid found in the ash from the total weight obtained, and report the difference as the true ash of the substance. A similar correction is often made for the "sand and carbon" left on treating the ash with dilute acid, the sand being merely an accidental impurity, and not a true constituent of the plant, and the carbon being simply due to incomplete combustion of the organic matter.

100. THE ORDINARY CONSTITUENTS of the ash of natural organic substances are potassium, sodium, calcium, magnesium, manganese, and iron, which exist as oxides, carbonates, sulphates, phosphates, silicates, and chlorides. Traces of other elements exist normally in certain cases, but the foregoing are those to which attention is generally directed. In *algæ*, notable traces of bromides and iodides occur, while *cryptogams* contain aluminium,[1] and barium has been found as a constituent of the ash of Egyptian wheat (*Jour. Chem. Soc.*, xxviii. 662). Minute traces of copper and some other elements (including rubidium, cæsium, and lithium) are said to be normally present in certain plants.

101. ANALYSIS OF THE ASH.—The determination of the constituents of the ash may be effected by the ordinary methods of mineral analysis, but it should be borne in mind that the ash of wheat and other cereals is apt to contain pyrophosphates, and these must be converted into orthophosphates, by fusing the ash with alkaline carbonate, before the ordinary process for the estimation of *phosphoric acid* can be employed. The determination of the *chlorine* volumetrically by silver nitrate (with potassium chromate as indicator) cannot be effected with accuracy, unless the phosphates have been previously removed by precipitating the aqueous solution of the ash with calcium nitrate.

102. In some cases it is of service to ascertain the proportion of

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[1] Flowering plants do not contain aluminium as a normal constituent, but *clay* is too common a substance for traces of silicate of aluminium not to occur occasionally in plant products.

the total ash which is *soluble in water*. This is most conveniently done by igniting and weighing the insoluble matter, and deducting the weight found from that of the total ash previously determined. The aqueous solution can then be used for the determination of the chlorides, "alkalinity," &c. Some analysts apply the term "soluble ash" to the ash left on igniting the residue obtained by evaporating to dryness the filtered aqueous solution of the substance. This is not identical with the *soluble portion of the ash* of the whole substance, and should be called in preference the "ash of the aqueous extract."[1]

The *alkalinity*, or capacity of the ash for neutralising acid, is often a useful indication. It is commonly expressed in terms of K_2O, and is estimated by titrating the filtered aqueous solution of the ash with standard acid. Champion and Pellet state that the amount of acid required to saturate the alkaline carbonates of the ash of a particular plant is practically constant.[2]

103. **Poisonous Metals** are apt to occur as impurities in certain commercial organic products, being accidentally introduced during the process of preparation. The objectionable metals most commonly occurring are *lead*, *copper*, *zinc*, and *tin*, and in ordinary cases the search may be limited to these elements.

104. LIQUIDS.—In some cases, as, for instance, vinegar and lemonade, the metallic impurities may be sought for in the original liquid, but in others it is desirable to evaporate the liquid carefully to dryness, ignite the residue, and test for the metals in the resultant ash. The evaporation should be conducted in porcelain. 100 c.c. of such liquids as beer, cider, or vinegar will usually suffice for the examination, but sometimes the use of considerably larger volumes is desirable. Towards the end of the evaporation, an addition of strong nitric and sulphuric acids should be made, the quantity used depending on the amount of organic matter to be destroyed. The evaporation is then carefully completed, and the residue ignited at a low red heat. After cooling, the ash is moistened with nitric acid and one drop of sulphuric acid, and

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[1] If a plant contained malate of calcium this would be dissolved by hot water, and hence would pass into the aqueous extract; but on igniting the residue obtained by evaporating the extract, the calcium malate would be converted into calcium carbonate, which is insoluble in water. Hence the "ash of an aqueous extract" may be insoluble in water.

[2] (*Jour. Chem. Soc.*, xxviii. 907, 1216.) They further state that if the ash of an entire plant be analysed, and the total potassium and sodium calculated to their equivalent of acid, a number is obtained which is constant for that particular plant, and similarly of the total calcium and magnesium. In other words, the bases contained in plants exhibit the same equivalent interchangeability that is remarked in silicates.

again ignited. It is then again treated with a few drops of nitric acid, which is evaporated off cautiously, the process being stopped directly acid fumes ceased to be copiously evolved. The residue is then treated with hot water, and the solution filtered, when the following scheme of analysis should be followed:—

<table>
<tr><td colspan="3">Aqueous Solution may contain copper, zinc, iron, &c. Add excess of ammonia and filter.</td><td colspan="2">Residue may contain lead, tin, &c. Wash, and pour boiling solution of ammonium acetate on the filter.</td></tr>
<tr><td rowspan="2">Precipitate may contain iron, phosphates, &c.</td><td colspan="2">Filtrate, if blue, contains copper. Divide into two portions.</td><td rowspan="2">Solution. Acidulate with acetic acid, and add potassium chromate. A chrome yellow precipitate indicates <i>lead</i>.</td><td rowspan="2">Residue. Ignite filter paper, fuse ash in porcelain crucible with potassium cyanide, dissolve product in water, filter, boil insoluble residue with strong hydrochloric acid, dilute, and treat clear solution with mercuric chloride. A white silky precipitate of mercurous chloride is due to <i>tin</i>.</td></tr>
<tr><td>1. Acidulate with acetic acid and add potassium ferricyanide. Brownish precipitate or coloration is indicative of <i>copper</i>.[1]</td><td>2. Heat to boiling, and add potassium. ferrocyanide. White precipitate or turbidity indicates <i>zinc</i>.</td></tr>
</table>

105. **Solids** may be examined for traces of the foregoing poisonous metals in precisely the same way as liquids which have been concentrated to a small bulk by evaporation.

The examination for arsenic and poisonous metals in cases of *suspected poisoning* does not come within the scope of this work, and will not be described.

The detection of *alum* and other mineral adulterants of flour and bread will be described in the sequel.

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[1] Exceedingly minute traces of copper are perhaps best detected by introducing a knitting needle into the slightly acidulated and tolerably concentrated aqueous solution of the ash, removing it after some hours, cautiously rinsing it in water, and then immersing it in dilute ammonia, with free contact of air. The copper precipitated on the iron will pass into solution, and may be detected by acidulating the ammoniacal liquid with acetic acid and adding potassium ferrocyanide, when a purple or brownish coloration will be produced, if a trace of copper be present.

ALCOHOLS.

106. The term "alcohol" is popularly applied to the pure essence or spirit which imparts to wine and other fermented liquids an intoxicating property. When used without qualification and as a proper name, it is to be understood as applying to ethyl alcohol or spirit of wine.

In modern chemistry, the word alcohol, in a *generic* sense, has a much wider meaning, being applied to a very numerous class of bodies, many members of which present a close resemblance to spirit of wine, while in others the properties which are characteristic of ordinary alcohol are conspicuous by their absence.

107. **An Alcohol** may be defined as a neutral compound of carbon, hydrogen, and oxygen, capable of reacting directly on acids with elimination of water and formation of ethers.

The only alcohols which will be fully described in this division of the work are—

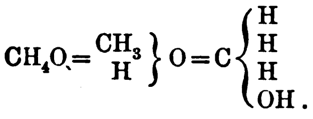
$CH_3.OH$. Methyl Alcohol, occurring in wood spirit;
$C_2H_5.OH$. Ethyl Alcohol, occurring in spirit of wine; and
$C_5H_{11}.OH$. Amyl Alcohol, occurring in potato spirit.

Glycerin, obtained by the decomposition of fats, has the constitution of a triatomic alcohol, and is fully considered in a subsequent section, in which reference is also made to *cetyl alcohol*, *myricyl alcohol*, *cholesterin*, &c.

Phenol and Cresol, which are sometimes regarded as phenyl and cresyl alcohols, are fully described in the sections referring to them, as also are the *sugars*, which have many of the characters of alcohols.

108. METHYL ALCOHOL.

Methylic Hydrate. Carbinol. Wood Spirit.



$$CH_4O = \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O = C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right..$$

Methyl alcohol may be prepared by a variety of synthetical reactions, but the distillation of wood is almost the only method of obtaining it possessed of practical interest.[1] Birch is the best wood for the purpose, after which come, in order of their respective value, beech, alder, and oak. The wood, thoroughly divested of its bark, is distilled in large iron retorts at a temperature of 400° to 500° F. The product of the distillation is run into tanks, and the tar allowed to separate. The aqueous liquid is neutralised with lime and redistilled, when impure acetate of calcium remains in the still, and crude pyroxylic spirit distils over. An intermediate distillation sometimes precedes the treatment with lime. The pyroxylic spirit is again rectified over slaked lime to remove acid, &c., the product treated with sulphuric acid to remove tar, and to neutralise ammonia and methylamine, the liquid redistilled, and in some cases rectified once or more over quicklime.[2]

109. The methylic alcohol contained in wood spirit can be separated in a state of tolerable purity by saturating the liquid with fused chloride of calcium, which combines with the methyl alcohol to form a compound of the formula $CaCl_2, 4CH_4O$, which is not decomposed at a temperature of 100° C. The mixture is, therefore, heated on the water-bath, by which the acetone and other constituents of the wood spirit are driven off, and may be collected, if desired. The residue is next distilled with water, when the compound of chloride of calcium and methyl alcohol is decomposed and the latter distils over; and may, if required, be rectified from quicklime in the same way as ordinary alcohol.

110. Pure methyl alcohol may be obtained by distilling 1 part of purified commercial wood spirit with 1 of sulphuric acid and 2 of acid oxalate of potassium. The receiver is changed as soon as crystals of methyl oxalate begin to form in the neck of the retort; and the process is then continued till the temperature of the mixture reaches about 170° C. Or the oxalate may be prepared by simply dissolving dehydrated oxalic acid in boiling methylic alcohol. The crystals of methyl oxalate are dried by pressure, treated with water, allowed to stand some time, and then redistilled, preferably with an addition of caustic soda, when pure dilute methyl alcohol is obtained, which may be rectified over quicklime or baryta.[3] A preferable plan is to saturate a solu-

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[1] Methyl alcohol is now obtained in large quantities from *vinasse*, the residue remaining after the distillation of fermented beet-root molasses.

[2] 100 parts of properly seasoned birch-wood usually yield 44 per cent. of crude acetic acid (containing 9 per cent. of glacial acid); 9 of tar; 24 of charcoal; about 22 of water; and from 0·5 to 1·2 of wood spirit.

[3] Traces of impurity which cause methyl alcohol to react with the iodoform

tion of benzoic acid in purified commercial wood spirit with hydrochloric acid gas, digest the mixture on the water-bath for a few hours and distil. The portion of the distillate which passes over above 100° C. is washed by agitation with cold water, and decomposed, by heating it in a flask attached to an inverted condenser, with a slight excess of caustic soda dissolved in three times its weight of water. The resultant methylic alcohol is then distilled off and rectified over lime. The benzoic acid may be recovered by treating the sodium benzoate with hydrochloric acid.

111. Pure methyl alcohol is a colourless mobile liquid of purely spirituous odour. (The empyreumatic odour of common wood spirit is due to impurities.) The boiling point, as given by different observers, varies from 55° to 66°·5, and apparently depends not inconsiderably on the nature of the containing vessel. Dupré gives the boiling point as 58°·6, Kopp obtained a mean of 54°·9, Vincent and Delachanel give 64°·8 as the boiling point of pure anhydrous methyl alcohol, while, according to Dittmar and Stewart, the perfectly anhydrous compound boils at 55°·1 C.

112. According to Dumas and Mitscherlich, the density of methyl alcohol is ·8142 at 0°, and ·7980 at 20° C. This gives a density of ·8061 at 10° C., which closely corresponds with the independent result of Deville, who obtained ·8070 as the density at 10° C. The mean of these results gives a calculated density of ·8021 at 15°·5 C. (=60° F.) Dupré's figures are very sensibly different. Duclaux, who experimented on a very pure product, obtained ·7995 as the density of methyl alcohol at 16° C.[1] It is doubtful, however, whether water at 16° C., at 4° C., or at 0° C. was taken as unity (see par. 14).

113. The difference between the densities of mixtures of methyl alcohol and ethyl alcohol with the same proportions of water is so small that for most purposes the alcohol tables in par. 156 may be used for ascertaining the strength of methyl alcohol. When accurate results are desired, and the sample contains a large percentage of alcohol, it is desirable to dilute it with twice its weight of water before taking the density, subsequently multiplying the percentage of methyl alcohol found by three.

114. Methyl alcohol is miscible in all proportions with water, ordinary alcohol, and ether. In its solvent properties and chemical reactions it presents the closest analogies to ethylic alcohol (par. 140).

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test may be destroyed by treating the spirit with one-tenth of its weight of iodine, adding excess of caustic soda solution, and distilling carefully.

[1] The boiling point was exactly 66° C., and each fraction distilled had precisely the same surface-tension (*Annales Chim. et Phys.*, 1878, xiii. 86).

115. By the oxidation of methyl alcohol formic acid, CH_2O_2, is produced, and this by farther oxidation is converted into carbonic acid.

Wood Spirit. Wood Naphtha. Pyroxylic Spirit.

French—Esprit de bois. *German*—Holzgeist.

116. These names are applied to the impure methyl alcohol of commerce.

The method of manufacturing wood spirit has already been described (par 109).

Wood spirit is a very complex liquid, containing variable proportions of methyl alcohol, acetone, methyl acetate and formate, dimethyl-acetal, allylic alcohol, aldehyde, water, &c. The following table shows the composition, densities, and boiling points of the more important of these bodies :—

		Specific Gravity.	Boiling Point. ° C.
Methyl alcohol, CH_4O	$-\left.\begin{matrix}(CH_3)\\H\end{matrix}\right\}O$	·8142 (·8021 at 15°·5 C)	55(?)
Methyl acetate, $C_3H_6O_2$	$-\left.\begin{matrix}(CH_3)\\(C_2H_3O)\end{matrix}\right\}O$	·9562	56·3
Acetone, C_3H_6O	$-\left.\begin{matrix}(CH_3)\\(C_2H_3O)\end{matrix}\right\}$	·8063 (at 11° C.) ·8140 (at 18° C.)	56·5
Dimethyl-acetal, $C_4H_{10}O_2$	$-\left.\begin{matrix}(CH_3)_2\\(C_2H_4)''\end{matrix}\right\}O_2$	·8555	65·0
Allyl alcohol, C_3H_6O	$-\left.\begin{matrix}C_3H_5.\\H\end{matrix}\right\}O$	·8709 (at 0° C.) ·8604 (at 13° C.)	96·5

The "tailings" contain furfurol, methyl-ethyl ketone, and allyl acetate, with small quantities of pyroxanthine.

The best commercial wood spirit contains about 95 per cent. of real methyl alcohol, the commoner varieties from 75 to 90 per cent., while some samples may contain only 35 to 40 per cent.

117. The density of crude wood spirit is not a certain indication of the proportion of methyl alcohol present, as its composition varies considerably. For dissolving resins, especially gum sandarac and mastic, painters choose naphtha holding some of the essential oils in solution. By treating crude wood spirit with lime, and again distilling, a product of low specific gravity is obtained containing little acetone and much methyl alcohol, but the menstruum for dissolving resins is prepared by distilling off the refined portion of the crude naphtha without employing lime. The former product has a low gravity and is miscible with water, but the latter is heavier, contains much acetone (see par. 126), and becomes milky on dilution from the separation of empyreumatic oils.

118. The odour of wood spirit is very characteristic. Wood

naphtha is quite unfit for drinking, being nauseous and highly deleterious. Pure methyl alcohol is free from these objections.

Commercial wood spirit gives a brown colour on heating with caustic alkali; mixed with concentrated sulphuric acid a red or reddish-brown colour is developed; and it reduces a solution of mercurous nitrate. These reactions distinguish wood spirit from pure methyl alcohol.

119. Assay of Wood Spirit. For producing dimethyl-aniline it is important that the wood spirit used should be as rich as possible in methyl alcohol, and contain but little of certain impurities, acetone being particularly objectionable (par. 123).

120. C. Bardy (*Jour. Pharm.*, [5] iv. 129) has described a method of estimating the proportion of real *methyl alcohol* in wood spirit, based on the amount of iodoform produced on treating the sample with iodine and caustic alkali. As, however, the formation of iodoform from pure methyl alcohol is open to grave question, the method is of very doubtful utility.

121. Krämer and Grodski have proposed to estimate the methyl alcohol in wood spirit by observing the vapour-density, the impurities having comparatively high molecular weights.

122. The proportion of *real methyl alcohol* in commercial wood spirit is most accurately determined by the following process, originally due to Krell and worked out by Krämer and Grodski, and also by Bardy and Bordet. A dry flask is furnished with a cork fitted with a tapped funnel or pipette and connected with an inverted condenser; 15 grammes of phosphorus di-iodide are placed in the flask, and 5 c.c. of the sample of wood spirit (measured at 15° C.) added slowly, drop by drop, by means of the pipette; 5 c.c. measure of hydriodic acid of 1·7 sp. gr., containing in solution 8·5 grammes of free iodine, is next added through the pipette. The flask is then heated to 80° or 90°C. by immersion in hot water for a few minutes, after which the condenser is placed in its ordinary position, and the contents of the flask are distilled and collected in a graduated tube. The distillate is shaken with water, and the volume of methyl iodide read off. Corrections of 8 volumes per 1000 must be made for the solubility of the methyl iodide in water, and for the loss due to the vapour which fills the apparatus. This error, which is constant for the same apparatus, is determined by distilling a known measure of iodide of methyl, measuring the distillate, and thus ascertaining the loss. Krell prefers to pass a current of air into the apparatus, through the pipette, and thus drive out the vapour of methylic iodide. Under these conditions, 5 c.c. of pure anhydrous methyl alcohol yield 7·45 c.c. of the iodide.

By the iodine process, any *methyl acetate* present in the sample is converted into iodide, and hence increases the apparent percentage of methyl alcohol. For most purposes, the error thus introduced can be neglected. If desired, the quantity present can be previously determined approximately by heating a known quantity of the wood spirit with standard soda, and titrating the excess with standard acid. 40 parts of NaHO neutralised correspond to 74 of methyl acetate, or 32 of methyl alcohol. The amount of methyl alcohol so found should be subtracted from the total amount corresponding to the iodide, in order to ascertain the real amount of methyl alcohol existing as such in the sample.

When *acetone* is present it distils over with the methyl iodide, and it is only by repeated washing with water that the distillate can be wholly freed from it. Bardy and Bordet have constructed a table showing the diminution in volume undergone by methyl iodide containing various percentages of acetone by washing with water. In the absence of the table, the error caused by the presence of acetone might be avoided by saponifying the washed distillate with alcoholic potash, evaporating to dryness, dissolving the residue in water, acidulating an aliquot part of the solution with nitric acid, and precipitating the iodide by silver nitrate. 235 parts of iodide of silver will represent 32 of methyl alcohol.

123. Methods for detecting and estimating *acetone* in wood spirit are described in par. 127 *et seq.* For the manufacture of colouring matters, the methyl alcohol should not contain more than 1 per cent. of acetone, as it not only hinders the methylating process but reduces the yield both of the volatile bases and the non-volatile ammonium compounds; the presence of one molecule of acetone causing a loss of one molecule of aniline. Besides, the base obtained from an article containing much acetone has properties which render it useless for the production of violet.

124. The *other constituents* of wood spirit when treated with iodide of phosphorus yield distillates soluble in water, or are converted into resinous bodies, with the exception of dimethylacetal, 5 c.c. of which yields 5·3 c.c. of methyl iodide.

For the preparation of the iodide of phosphorus, 15·5 grammes of phosphorus are dissolved in 350 c.c. of carbon disulphide, and 127 grammes of iodine are gradually added, the vessel being kept well cooled. The di-iodide separates in crystals, which are dried in a slightly warm current of air, and preserved in a well-stoppered bottle.

125. The detection of small admixtures of *ethyl alcohol* in

wood spirit is less important than the converse. The following tests have been proposed for the purpose :—

a. M. Berthelot heats the sample with twice its volume of concentrated sulphuric acid. If 1 per cent. of ethyl alcohol be present, ethylene is evolved, and may be absorbed by bromine and estimated as $C_2H_4Br_2$. Acetone and the normal impurities of wood spirit may yield CO and CO_2, but not ethylene.

b. Another very delicate test is based on the fact that ethyl alcohol forms iodoform when treated with iodine in presence of an alkali—a reaction which is not common to pure methyl alcohol. As, however, acetone and many other bodies act in the same way as ordinary alcohol, the test becomes practically one for the purity of methyl alcohol, rather than for the detection of ethyl alcohol in the commercial product.

c. Riche and Bardy (*Compt. rend.*, lxxxii. 768) use a reaction dependent on the production of aldehyde from ethylic alcohol by oxidising agents, and the reaction of aldehyde, methylal, acetal, &c., on salts of rosaniline, whereby a violet colouring matter is produced, which is not destroyed by subsequent addition of sulphurous acid. 4 c.c. of the liquid to be examined are mixed with 6 c.c. of concentrated sulphuric acid and 10 c.c. of water. 7 or 8 c.c. are distilled into 10 c.c. of water, and to this liquid are added 5 c.c. of sulphuric acid, and 10 c.c. of a solution of potassium permanganate of 1·028 sp. gr. After five minutes have elapsed, 4 c.c. of a solution of sodium thiosulphate, of 1·29 sp. gr., and 4 c.c. of a solution of magenta, containing 0·02 gramme per litre, are added. Under these conditions, wood spirit unmixed with ethyl alcohol gives a yellowish-white liquid, but if ethyl alcohol be present the solution assumes a violet colour of greater or less intensity. Acetone, formic acid, and isopropyl alcohol give no similar reaction.

126. **Acetone.** Acetic Ketone. Pyro-acetic Spirit.

$$C_3H_6O = \left.\begin{array}{c} CH_3 \\ C_2H_3O \end{array}\right\} = \left\{\begin{array}{l} CH_3 \\ CO(CH_3). \end{array}\right.$$

Acetone occurs largely in some varieties of wood spirit, and is a constant product of the dry distillation of acetates. It is also obtained from the residue left after manufacturing aniline by the distillation of nitro-benzene with acetic acid and iron.[1] Acetone is a colourless limpid liquid of peculiar ethereal odour and burning taste. It is miscible in all proportions with ether, alcohol, and water. It dissolves nearly all resins, gums, camphor, and fats. Gun-cotton dissolves in it with facility. Acetone has many of the properties of the aldehydes, and like them readily unites with the acid sulphites of the alkali metals to form crystalline compounds. This fact may be employed for its detection. Caustic potash and dry calcium chloride are insoluble in acetone, a fact which distinguishes it from methyl alcohol.

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[1] Some specimens of commercial acetone leave, on distillation, a yellowish-brown residue with alkaloidal properties, and having a physiological action similar to the ptomaines.

127. The presence of much acetone in wood naphtha may be detected by mixing the sample with twice its measure of a *saturated* aqueous solution of calcium chloride, when the acetone separates, and forms a layer at the surface of the liquid. The test becomes more delicate if, instead of employing a solution, *powdered* calcium chloride be added to the naphtha.

A more delicate reaction is that of J. E. Reynolds, described in par. 134, the success of the test for the detection of wood spirit depending on the presence of acetone in the latter.

128. The proportion of acetone present in wood spirit may be determined by the following method, dependent on the formation of iodoform. 1 c.c. of the sample of wood spirit is mixed with 10 c.c. of a solution containing 80 grammes of caustic soda in 1 litre. After agitating, 5 c.c. are added of a solution containing 254 grammes of iodine and 332 of iodide of potassium in 1 litre. The whole is again agitated, and the iodoform which separates is dissolved by shaking with 10 c.c. of ether free from alcohol. The ethereal layer is allowed to separate, and is then withdrawn and evaporated at the ordinary temperature, the residue of iodoform being subsequently dried for a short time over sulphuric acid, and weighed. The ether could probably be advantageously replaced by well-washed chloroform. 394 parts of iodoform correspond to 58 of acetone.

129. **Allyl Alcohol.**—$C_3H_6O = C_3H_5.OH = CH_2{:}CH.CH_2.OH$. This substance occurs as a constituent of wood spirit, and appears to be a legalised substitute in Germany for wood spirit for "methylating" alcohol (see next paragraph). Pure allyl alcohol as a liquid of penetrating odour, boiling at 96° to 97° C., and miscible in all proportions with water. It is readily and even violently oxidised by chromic acid mixture (par. 255), a strong smell of acrolein, C_3H_4O, being observable, which body subsequently undergoes further oxidation. The aqueous solution of allyl alcohol readily decolorises bromine water, with formation of an additive product of the composition $C_3H_6Br_2O$.

130. **Methylated Spirits of Wine** is a mixture of 90 per cent. of rectified spirit (ethyl alcohol) with 10 per cent. of commercial wood spirit.[1] The acetone and other constituents of

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[1] Under an Act which came into force at the commencement of 1881, the

the wood naphtha are so difficult to remove that the spirit is considered to be permanently unfitted for drinking purposes, and therefore is not subject to duty. By rendering methylated spirit absolute, however, the impurities may be so far eliminated that the resultant alcohol is not wholly disqualified for drinking use, and hence the Excise have disallowed the sale of absolute methylated alcohol. For laboratory purposes, ordinary methylated spirit may be greatly improved by digesting it for some days with caustic potash or soda, and then distilling. The alkali converts aldehyde and acetone into resinous bodies, and saponifies the methyl acetate, so that after distillation the liquid contains little besides methyl and ethyl alcohols.[1]

131. As methyl alcohol has a sensibly lower boiling point than ethyl alcohol, methylated spirit boils at an intermediate temperature, a fact which has been utilised for a rough examination of methylated spirit. The following data are due to Dr Ure:—

	Boiling Point. °C. Wood spirit.	Alcohol.
Density of 0·870, . . .	62·2	82·2
Density of 0·832, . . .	60·0	77·2

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methylated spirit in Germany is made by adding 5 per cent. of wood spirit, percussion-cap makers and colour-varnish makers being allowed to use an article to which ½ per cent. of turpentine or ¼ per cent. of animal oil has been added instead of the wood spirit. Only such wood spirit may be used as has been sanctioned by the authorities, and has remained in bond until required for use. The wood spirit must be tested as to its specific gravity, boiling point, miscibility with water, behaviour with soda solution, and power of decolorising bromine. The last test is admitted to be unsatisfactory.

[1] The following conclusions were adopted by a Committee of the United States National Academy of Sciences in a recent Report, to the Commissioner of Internal Revenue, on Methylated Spirit for manufacturing. By treating a mixture of 10 per cent. of wood spirit and 90 per cent. of ethyl alcohol with bone-black, filtering, and then distilling with the aid of a fractionating arrangement, the principal product obtained is nearly free from methyl alcohol, and the odour and taste of this body are not very marked, and can only with difficulty be recognised by those unskilled in such matters, but are easily perceived by experts. The spirit thus purified might be used in the manufacture of low-grade whisky and rum; but, as the process of purification necessarily involves very careful distillation, it would be as difficult to purify methylated spirit surreptitiously on a large scale as it is at present to carry on the illicit manufacture of non-methylated alcohol. Cazeneuve and Chapuis state that by the action of a copper-zinc couple at 70° C. during five or six days methylated spirit may be entirely deprived of its disagreeable odour. By more prolonged treatment the change can be effected in the cold. The effect is due to the conversion of the acetone contained in the crude wood spirit into iso-propyl alcohol. By distilling the spirit thus treated from a water-bath a nearly odourless product may be obtained.

Hence it appears that an addition of 10 per cent. of wood naphtha to alcohol lowers the boiling point 3°·3 C. (=6° F.).

132. METHYLATED FINISH is a preparation sold by those who are not licensed as vendors of methylated spirit. It is made by dissolving a gum-resin in methylated spirit, and the Excise insists that the proportion present shall not be less than 3 ounces in the gallon.

133. **Detection of Methyl Compounds in Alcoholic Liquids.**—In consequence of the cheapness of methylated spirit as compared with pure ethyl alcohol, there is a great inducement to substitute the former in tinctures and other preparations which should only contain the latter. On this account it is frequently important to test alcohol for an admixture of wood spirit, and various methods have been devised for the purpose, some founded on the detection of methyl alcohol itself, and others on the recognition of acetone, which appears to be constantly present in commercial wood spirit.

134. *a.* The following process for testing alcohol depends on the presence of acetone, and was devised by J. E. Reynolds:—"Take 200 c.c. of the spirit, and rapidly distil off 50 c.c.; dilute the distillate with an equal volume of water, and slightly warm with addition of a few c.c. of solution of potassium hydrate. On cautious addition of mercuric chloride, the oxide at first thrown down is speedily redissolved; excess of the mercuric salt must be carefully avoided. The alkaline liquid should be filtered clear, much of the alcohol allowed to evaporate slowly, and the residue then divided in two portions. One part is to be violently boiled for a few minutes; a yellowish-white gelatinous precipitate will suddenly make its appearance if the acetone compound be present. In the second portion, dilute acetic acid, when added in excess, should produce a bulky, white, gelatinous precipitate, containing, when washed and completely dried, between 78 and 79 per cent. of mercury."

135. *b.* P. Cazeneuve distils 100 c.c. of the spirit, and collects each 10 c.c. of the distillate in separate cylinders. To each fraction he then adds 1 c.c. of a solution containing 5 grammes of potassium permanganate per litre. If the sample contained wood spirit, each fraction instantly reduces the permanganate with brown coloration, owing to the presence of acetone in all the distillates. If the alcohol be free from methyl compounds, but contains an appreciable quantity of aldehyde, the first two fractions will reduce the permanganate at once, but the following portions react less rapidly. This distinction is due to the low boiling point of aldehyde causing it to become concentrated in the first portions of the distillate.

136. *c.* The following process has been devised by MM. Riche and Bardy for the detection of methyl alcohol in commercial spirit of wine. It depends on the formation of methyl aniline violet. 10 c.c. of the sample of alcohol, previously rectified if necessary over potassium carbonate, are placed in a small flask with 15 grammes of iodine and 2 grammes of red phosphorus. Methyl and ethyl iodides are formed, and should be distilled off into about 30 c.c. of water. The heavy oily liquid which settles to the bottom is separated from the water and transferred to a flask containing 5 c.c. of aniline. The flask should be placed in cold water, in case the action should be violent; or, if necessary, the reaction may be stimulated by gently warming the flask. After one hour the product is boiled with water and solution of soda added, when the bases rise to the top as an oily layer, which may be drawn off with a pipette after filling the flask with water up to the neck. 1 c.c. of the oily liquid thus obtained is next oxidised by adding it to 10 grammes of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate. After being thoroughly mixed, the whole is introduced into a glass tube and heated to 90° C. for eight or ten hours. The product is exhausted with warm alcohol, the liquid filtered, and made up with alcohol to 100 c.c. If the sample of spirit were pure, the tint of the liquid is red, but in presence of 1 per cent. of methyl alcohol it has a distinct violet shade; with 2½ per cent. the shade is very distinct, and still more so with 5 per cent. To detect more minute quantities of methyl alcohol, 5 c.c. of the coloured liquid are diluted to 100 c.c. with water, and 5 c.c. of this again diluted to 400 c.c. The liquid thus obtained is heated in porcelain, and a fragment of white merino (free from sulphur) immersed in it for half an hour. If the alcohol were pure the wool will remain white; but if methylated, the fibre will become violet, the depth of tint giving a fair approximate indication of the proportion of methyl alcohol present.

137. *d.* The following process is due to J. T. Miller. In the case of tinctures and other liquids containing fixed matters, the greater part of the spirit should be distilled off and the test applied to the distillate. The method is based on the fact that methyl alcohol produces formic acid when treated with oxidising agents, but that ethyl alcohol yields a mere trace of the same body. Nevertheless, the fact must not be overlooked that a *trace* of formic acid (or other reducing agent) is formed, even when pure ethyl alcohol is operated on. 3 grammes of bichromate of potassium and 2½ c.c. of concentrated sulphuric acid are mixed in a small tubulated flask with 25 c.c. of water and 3 to 4 c.c. of

the spirit to be tested. After standing for a quarter of an hour, the flask is attached to a condenser and the mixture is distilled. When 25 c.c. have passed over, the acid distillate is treated with a very slight excess of sodium carbonate, boiled down to about 10 c.c., and enough acetic acid added to impart a distinct, but feeble, acid reaction. The liquid is then treated with 0·1 gramme of silver nitrate dissolved in about 3 c.c. of water, and the whole gently heated for two or three minutes. If the solution merely darkens a little, but continues quite transparent, the spirit is free from methylic alcohol; but if a copious precipitate of dark brown or black metallic silver separates, and the tube, after being rinsed out and filled with clean water, shows a distinct film of silver, which appears brown by transmitted light (best seen by holding it against white paper), the spirit is methylated.

138. The accurate *determination* of methyl alcohol in presence of ethyl alcohol is very difficult.[1] A. Dupré has described (*Analyst*, i. 4) the following method of detecting and approximately estimating the amount of methyl alcohol in spirituous liquids:—Five ounces of the spirit are distilled twice, the liquid having been rendered alkaline the first and acid the second time, about two-thirds being passed over each time. The distillate is next shaken with dry potassium carbonate, and allowed to stand twelve hours. The upper layer is then removed with a pipette, and again twice distilled, about an ounce being driven over the first, and half an ounce the second time. This last half-ounce will contain any methylic alcohol present in the original five ounces of the sample.

All the distillations should be conducted in an apparatus having all the parts air-tight, expansion of the contained air being allowed for by a mercury valve. In this way the distillation can be effected without loss. About one-third of the last distillate is next diluted with about six times its measure of water, and in this spirituous liquid the alcohol is carefully determined, first by the density (see par. 154), and subsequently by oxidation to acetic acid, with estimation of the latter by titration with alkali. With pure alcohol, both methods should give results agreeing within 0·1 per cent. In presence of methyl alcohol, the oxidation process gives a sensibly lower result, as no fatty acid is formed by its oxidation. If any appreciable quantity of methyl alcohol be present, on opening the flask in which the oxidation is performed, a slight escape of gas will take place, owing to the carbon dioxide produced. With pure ethyl alcohol, on the contrary, a partial vacuum is formed. In a whisky to which 10 per cent. of methylated spirit was added, the specific gravity method gave 10·08 per cent. of alcohol in the diluted distillate, against 9·50 per cent. by the chromic acid method. A determination of the alcohol by Geissler's vaporimeter affords a useful check. Thus, the same whisky above mentioned gave 10·45 per cent. of alcohol by this process, owing to the presence of methyl alcohol increasing the tension of the vapour. The remainder of the distillate in which the methyl alcohol has been concentrated may be examined for that body by the tests described in pars. 136 and 137.

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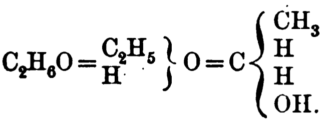
[1] A process has been described by Hager for determining the proportions of methylic and ethylic alcohol existing in a mixture, by converting them into the corresponding oxalates by distillation with potassium oxalate and strong sulphuric acid. The methyl oxalate, $(CH_3)_2C_2O_4$, so obtained is a solid crystalline body, while the ethyl oxalate, $(C_2H_5)_2C_2O_4$, is a liquid. Although, when in an unmixed state, mere traces of methyl alcohol can be detected by the above reaction, the presence of ethyl alcohol in the sample, and, consequently, of ethyl oxalate in the product of distillation, renders the method useless, as the crystalline methyl oxalate remains dissolved in the homologous liquid ether. Methyl oxalate, however, is soluble in water, while ethyl oxalate is practically insoluble. Hence, by shaking the distillate with water, and determining the oxalic acid produced by its treatment with caustic alkali, it was thought possible that a practical process might be obtained. The experiments made by the writer in this direction ended in complete failure, very considerable quantities of ethylic oxalate always passing into the aqueous solution, although care was taken not to leave the oily layer in contact with the water for any length of time.

139. From researches by M. Duclaux, on the surface-tensions of the alcohols (*Annales Chim. et Phys.* [5], xiii. 76), it appears extremely probable that methyl alcohol could be detected, and even approximately determined, in spirituous liquids by simply noting the number of drops of the sample delivered by a pipette constructed to deliver 100 drops of water. A liquid containing 20 per cent. by volume of ethylic alcohol will give 176 drops, while methylic alcohol of the same strength will give only 147·5 drops.

140. ETHYL ALCOHOL.

Alcohol. Ethylic Hydrate. Methyl Carbinol. Spirit of Wine.

French—Alcool; Esprit de vin. *German*—Alkohol; Weingeist.



$$C_2H_6O = \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O = C\left\{\begin{matrix} CH_3 \\ H \\ H \\ OH. \end{matrix}\right.$$

Ethyl alcohol is the pure essence or spirit which imparts to wine and other fermented liquids an intoxicating property.

When used without qualification, and as a proper name, the term *alcohol* is to be understood as applying to ethyl alcohol, or "spirit of wine."

141. Pure anhydrous or "absolute" ethyl alcohol is a limpid, colourless liquid, of a penetrating and agreeable odour and hot pungent taste. Alcohol volatilises rapidly at ordinary temperatures, boils at 78°·4 C. (=173°·1 F.) and solidifies at −130°·5 C.

142. The density of alcohol has been determined by a variety of observers, whose results differ somewhat from each other, chiefly owing to the great difficulty with which the last traces of water are removed. The specific gravity is usually stated to be ·79381 at 60° F. (=15°·5 C.), water at the same temperature being taken as unity, but the recent labours of E. R. Squibb (*Ephemeris*, ii. 522; *Pharm. Jour.* [3], xv. 22) have shown that pure alcohol is obtainable of as low a density as ·79350, and that possibly even this product is not absolutely free from water. Hence alcohol of ·79381 sp. gr. really contains about 0·1 per cent. of water, an impurity so trifling in amount as not materially to vitiate the accuracy of the tables ordinarily relied on for calculating the strength of alcoholic liquids from the density.[1]

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[1] The following note on the history of alcohol tables is epitomised from the article of Dr. Squibb referred to in the text:—"The investigations of Gilpin for the British Government from 1788 to 1794, brought the specific gravity of absolute alcohol to ·7939 at 60° F., compared with water at the maximum density. Fownes and Drinkwater independently went over the subject some fifty years later, and respectively found the specific gravity to be ·7938 and ·79381 to 60° F., compared with water at the same temperature. Kopp is often quoted as an authority for the specific gravity of alcohol, but the best results given by him are considerably above those of earlier or later observers, and it is doubtful whether he supposed that he obtained anhydrous alcohol. Mendelejeff, in an admirable research published in 1865, brought the corrected specific gravity of alcohol to ·79367 at 15° C., compared with water at 4° C., a result which is practically in accord with Fownes and Drinkwater. Tralles, in 1811, adopting Gilpin's researches as far as they went, deduced a density of ·7939 at 15° C., compared with water at 4° C. This was nearly correct from his data, but he does not use this, and does use instead, as the basis of all his work, an erroneous equivalent to it. He states that this figure is equivalent to ·7946 at 60° F., compared with water at 60° F., whereas ·79411 is the true density of alcohol at 60° F. (=15°·5 C.), compared with water at the same temperature, if ·7939 be the density at 15° C., compared with water at 4° C. Gay Lussac, in 1824, practically reaches the same error as Tralles, which he appears to adopt from Rudberg, giving ·7947 as the density at 15° C (=59°F.), compared with water at 15° C., erroneously supposing that this was the temperature of the maximum density of water. All Gay Lussac's voluminous tables are vitiated by these errors. Stampfer, who appears to be a commonly accepted German authority, gives the density ·7951 at 15° C., compared with

143. Absolute alcohol burns with a whitish flame, which deposits carbon on a cold surface held in it. If the alcohol contain water, the flame produced is quite blue.

144. Alcohol is miscible with water in all proportions, a considerable evolution of heat and contraction in bulk taking place on admixture. The whole of the water can be removed from it with great difficulty only; even repeated distillation with the ordinary condensing arrangement does not remove the last 8 or 10 per cent. (sp. gr. ·8228).[1] By repeated treatment with carbonate of potassium or quicklime, with subsequent distillation, all but a minute trace of water may be removed from alcohol, which is then said to be "absolute." In commerce, several different strengths of "absolute alcohol" are recognised, the term being applied to any stronger spirit than can be obtained by mere distillation.

The presence of as small a proportion as 0·5 per cent. of water in alcohol is indicated by the pink colour assumed by the liquid on introducing a crystal of potassium permanganate. A less delicate test consists in agitating the alcohol with a little anhydrous cupric sulphate (made by gently igniting the powdered crystals), when the salt will acquire a blue colour if a notable quantity of water be present.

145. Absolute or very strong alcohol is powerfully poisonous, destroying the vital functions of the tissues by abstracting their moisture. For a similar reason, strong alcohol is a powerful antiseptic.

Alcohol is a powerful solvent for fluid and solid bodies, dissolving resins, volatile oils, camphor, phenol, creasote, glycerin, and numerous salts, acids, and organic bases. As a rule, the metallic chlorides, bromides, iodides, acetates, &c., are soluble in alcohol; while the carbonates, borates, sulphates, phosphates, oxalates, tartrates, malates, &c., are insoluble.[2]

Sulphur and phosphorus are slightly soluble in alcohol.

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water at the same temperature, a figure which is still more inaccurate than those of Tralles or Gay Lussac. Tralles' inaccurate tables are established by law as the basis of the Inland Revenue work both in Great Britain and the United States. although the error from the truth, as established by Fownes, Drinkwater, and Mendelejeff is about ¼ per cent."

[1] By attaching to the distillation-flask a long, wide glass tube, arranged vertically and filled with solid glass beads, Hempel obtained alcohol of 95 per cent. by slowly distilling spirit of 18 per cent.

[2] Most deliquescent salts, except potassium carbonate, are soluble in alcohol Inorganic compounds, if insoluble or sparingly soluble in water, are also insoluble in alcohol.

Iodine is readily soluble with brown colour; on addition of alkali the liquid is decolorised with formation of iodoform.

Alcohol absorbs many gases with considerable avidity. Some of them, such as hydrochloric and nitrous acids, decompose it with formation of the corresponding ethers (ethyl chloride, C_2H_5Cl, and ethyl nitrite, $C_2H_5NO_2$).

Concentrated nitric and chloric acids act very violently on alcohol, forming aldehyde, acetic acid, and other products. Chromic acid and permanganate of potassium react similarly.

Sulphuric, arsenic, and phosphoric acids react on alcohol, with production of ethyl acids. When the liquid is heated, ethylene gas or ordinary ether results, according to the boiling point of the liquid. Acetic, formic, oxalic, hydrochloric, and other acids decompose absolute alcohol with the formation of the corresponding ethers.

Bromine and chlorine act on absolute alcohol by removing part of the hydrogen and forming substitution-products (chiefly bromal and chloral).

Potassium and sodium dissolve in absolute alcohol, forming potassium and sodium ethylates (C_2H_5KO and C_2H_5NaO), which are decomposed by water into alcohol and caustic alkalies. B. W. Richardson has proposed to employ an alcoholic solution of sodium ethylate as a caustic.

146. **Rectified Spirit of Wine** is the name given to the most concentrated alcohol producible by ordinary distillation. The rectified spirit of British Pharmacopœia is described as containing 84 per cent. by weight of real alcohol, and having a density of ·838.

147. **Proof Spirit** of the British Pharmacopœia has a density of 0·920, which corresponds to a strength of about 49 per cent. by weight of real alcohol. The term "proof spirit" is very confusing to many people, and might with advantage be abandoned. Of this there is little chance at present, as it is adopted in several Acts of Parliament, and is the scale to which Sykes' hydrometer, used by the Excise, has reference. The Excise formerly tested the strength of spirits by pouring a certain amount on gunpowder. A light was then applied. If the spirit was above a certain strength ("proof") the gunpowder ultimately inflamed, but if weaker the gunpowder was too much moistened by the water to be capable of explosion, and the sample was said to be "under proof." By Act of Parliament, proof spirit is now defined to be a liquid of such density that, at 51° F., 13 volumes shall weigh the same as 12 volumes of water at the same temperature. The "proof spirit" thus produced

has a density of ·91984 at 15°·5 C. (= 60° F.), and contains, according to Fownes, 49·24 per cent. by weight of alcohol and 50·76 of water. Spirits *weaker* than the above are described by the Excise as being so many degrees, or so much per cent., "under proof" (U.P.). Thus, by the term "spirit of 20 per cent., or 20 degrees, under proof," is meant a liquid containing, at 60° F., 80 measures of proof spirit and 20 of water. "Spirit of 50° U.P." contains equal measures of proof spirit and water, while pure water is 100° under proof.

On the other hand, spirituous liquids *stronger* than proof spirit are described according to the number of measures of proof spirit 100 volumes would yield when suitably diluted with water. Thus, "spirit of 50° O.P." is alcohol of such strength that 100 measures at 60° F., when diluted with water to 150 measures, would be proof spirit.[1] Absolute alcohol accordingly is 75¼° O.P., and contains 175¼ per cent. of proof spirit, for 100 volumes when diluted with water would yield 175¼ volumes of spirit at "proof."

The relationship of percentages of absolute alcohol to those of proof spirit are explained further in par. 158.

148. In the United States, Tralles' tables are legalised, and consequently the proportion of alcohol in spirit is usually stated in percentage by volume; but a "proof spirit" is also recognised by the American Excise, which is defined as "that alcoholic liquor which contains one-half its volume of alcohol of a specific gravity of ·7939 at 60° Fahrenheit." The specific gravity of such spirit is stated to be ·93353 at 60° F., water at its maximum density being taken as unity. (This will correspond to a density of about ·9341 if water at 60° F. be taken as unity, and to a content of 42·7 per cent. by weight of absolute alcohol.) Absolute alcohol would contain 200 per cent. of proof spirit according to the U.S. Excise, instead of 175¼ per cent. as in the English system.

In the United States Pharmacopœia three different strengths of alcohol are recognised, namely:—(1) "Absolute alcohol;" (2) "Alcohol," specific gravity ·820 = 91 per cent. by weight; and (3) "Diluted alcohol," specific gravity ·928; made with equal measures of "alcohol" (No. 2) and water. This preparation corresponds closely to "proof spirit, B.P."

149. The "Spirit" of the German Pharmacopœia has a density of ·830 to ·834, corresponding pretty closely with "rectified spirit, B.P." The "Dilute Spirit," has a density of ·892 to ·896.

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[1] Owing to the contraction which occurs on mixing alcohol with water, the volume of water which it would be necessary to add in this instance would be considerably *more* than 50 measures. Thus, a mixture of 100 volumes of absolute alcohol with 60 of water only measures 154 volumes instead of 160.

150. **Examination of Commercial Alcohol.**—Ordinary spirit of wine is commonly assumed to consist of pure ethylic alcohol, more or less mixed with water. This, however, is frequently far from true, commercial ethylic alcohol often containing distinct traces of higher homologues, of aldehyde and acetic acid, of volatile oils, and of various fixed impurities, both organic and inorganic. *Methylated spirit of wine* is an acknowledged mixture of ethyl alcohol and *wood spirit* (par. 130). For the detection of the latter body in alcoholic liquids in which its unacknowledged presence is suspected, see par. 133 *et seq.*

The other common impurities of commercial alcohol may be sought for in the following manner:—

Amylic Alcohol and *fusel oil* may be detected by the methods described in par. 271 *et seq.*

Fixed Impurities may be detected and estimated by evaporating to dryness 50 or 100 c.c. of the spirit, and weighing the residue, if any. The proportion of inorganic matter can be ascertained by igniting the residue carefully at a low red heat. Some idea of the nature of the organic matter may be obtained by smelling the fumes produced when the residue is first heated.

Oily and Resinous Matters may be detected by diluting the spirit somewhat largely, when they are precipitated, and impart a milky appearance to the liquid.

Acetic Acid will be indicated by the acid reaction of the spirit.

Aldehyde imparts a peculiar flavour to the spirit. When present in quantity the spirit becomes brown when heated with caustic alkali. A smaller quantity is detected by adding a few drops of solution of argentic nitrate and exposing the liquid to a good light for twenty-four hours, when the silver will be reduced and deposited as a black powder if aldehyde or other reducing agent be present. Traces of aldehyde, &c., are nearly always present in commercial samples of alcohol. The British Pharmacopœia directs the silver test to be made by adding 30 fluid grains (2 c.c.) of decinormal argentic nitrate to 4 fluid ounces of the sample to be tested. After exposure to the light for twenty-four hours, and decantation from the black precipitate, no further reduction of silver should occur on repeating the treatment. A negative result on adding more silver solution and again exposing the liquid to light, proves the absence of a greater proportion of reducing agents per pint of spirit than can decompose about 2½ grains of nitrate of silver.

The proportion of *water* present in commercial alcohol may be deduced with accuracy from the specific gravity of the liquid (par. 154).

151. **Detection of Alcohol.**

When tolerably concentrated, alcohol is readily recognised by its physical properties, after previous distillation if necessary.

Methods for detection of alcohol in wood spirit are described on page 47.

In a dilute state, the following tests for alcohol are of service :—

a. J. Hardy detects small quantities (1 per cent.) of alcohol in aqueous liquids by shaking the sample for a few minutes with a small quantity of powdered guaiacum resin taken from the interior of a lump. The liquid is filtered, and few drops of hydrocyanic acid and a drop of weak solution of sulphate of copper added. In presence of alcohol a blue colour is produced, far more intense than is due to the slight colour of the solution of copper. When the alcohol is present in but small quantity, the tube should be viewed over white paper, and a blank experiment with distilled water made side by side with the sample. The author has verified this test.

b. E. W. Davy detects 0·1 per cent. of alcohol in water by adding a few drops of the liquid cautiously to a solution of 1 part of molybdic acid in 10 of strong sulphuric acid, gently warmed in a porcelain capsule. A blue coloration appears immediately, or after a few moments. Other alcohols, ether, and aldehyde give the same reaction, but chloroform and chloral hydrate do not. The author has proved the delicacy of this test to the above-named extent.

c. A very delicate test for small quantities of alcohol is that of Lieben, as modified by Hager (*Zeits. Anal. Chem.*, ix. 492). It depends on the fact that alcohol under the influence of iodine and an alkali yields iodoform, CHI_3, the properties of which are very characteristic. To 10 c.c. of the clear suspected liquid, five or six drops of a 10 per cent. solution of caustic potash or soda are added, and the liquid is warmed to about 50° C. A solution of iodide of potassium, fully saturated with free iodine, is next added drop by drop with agitation, until the liquid becomes permanently yellowish-brown, when it is carefully decolorised by a further cautious addition of the caustic alkali solution. If alcohol were present, iodoform is gradually deposited at the bottom of the tube in yellow crystals, which, after standing, may be examined with a lens. Under a microscopic power of 300 diameters its appearance is very characteristic, the usual forms being hexagonal plates, stars, and rosettes. Spirit diluted with 2000 parts of water, when treated as above and allowed to stand 12 hours, gives a distinct dust-like deposit of iodoform. The author has verified this test.

When chloroform and similar liquids are to be examined, 2 c.c. should be shaken with 10 c.c. of water, and the liquid passed through a wet filter, the test being applied to the filtrate.

Unfortunately, this very delicate reaction is not peculiar to alcohol, being produced also by acetone, aldehyde, isopropyl alcohol, propylic and butylic alcohols and aldehydes, various ethers, meconic, lævulic and lactic acids, turpentine, sugar, &c. On the other hand, it is not given by pure methyl or amyl alcohol, chloroform, chloral, glycerin or ether; nor by acetic, formic, or oxalic acid.

d. J. C. Thresh (*Pharm. Jour.* [3] ix. 408) has described a method of detecting and estimating small quantities of alcohol which is based on its oxidation to aldehyde by a mixture of bichromate of potassium and dilute sulphuric acid. It is evident that excess of the oxidising mixture must be avoided, or the aldehyde will be wholly converted into acetic acid, as actually occurs in Dupré's modification of the method, as described on page 70. The inventor of the process claims that it is capable of giving approximate quantitative results with a liquid containing ·04 to ·40 per cent. of alcohol, and that it will detect with certainty ·01 per cent. The following are the details of the method:—

100 c.c. of the dilute alcoholic liquid are placed in a small flask, together with 2 c.c. of a cold saturated solution of bichromate of potassium and 12 c.c. of normal sulphuric acid. A few pieces of pumice are added to prevent bumping, a bent tube attached, and 20 c.c. distilled off slowly into a graduated tube containing 3 c.c. of a syrupy solution of caustic soda. The distillate is then heated, kept at the boiling point for a few seconds, and placed aside for two hours. If the original spirituous liquid contained ·10 per cent. of alcohol, the contents of the tube will have acquired a deep yellow colour and have deposited flocks of aldehyde resin; with ·05 per cent. no resin separates, but the fluid is deep yellow and perceptibly opalescent; with ·01 per cent. the colour is only just perceptible, but the characteristic odour is still very distinct. Dr. Thresh employs the method colorimetrically by comparing the depth of colour with that produced by a liquid containing a known amount of aldehyde. His test experiments show that the method is approximately accurate within the limits named, and may be applied to the determination of alcohol in essential oils, urine, &c.

152. For the detection of alcohol in transparent soaps, Jay treats 50 grammes of the finely divided sample in a 200 c.c. flask, with 30 c.c. of strong sulphuric acid, and agitates till decomposition is complete. He then fills up the flask with water, separates the layer of fatty acids, nearly neutralises the aqueous liquid, and distils. The first 25 c.c. of the distillate are then examined for alcohol by the method of Riche and Bardy (par. 136).

153. Determination of Alcohol.

The estimation of alcohol in admixture with wood spirit, amyl alcohol, chloroform, ether, &c., may be effected by the methods described in the sections devoted to these substances.

In by far the greater number of instances the determination of alcohol is effected by *separating it from fixed substances* by distillation, and then ascertaining the proportion of alcohol present in the spirituous liquid condensed. This is practically the

154. Determination of Alcohol in mixtures consisting essentially of Alcohol and Water only.

1. This is most generally effected by accurately ascertaining the specific gravity of the mixture. From the specific gravity, the percentage of real alcohol is readily ascertained by reference to tables, on the construction of which great care has been bestowed by various observers, the subject being of great importance for Excise purposes. By the Excise, a glass or metal hydrometer is employed, the temperature of the liquid being carefully noted. In the laboratory, the specific gravity bottle is a more satisfactory and accurate instrument. In all cases the bottle must be filled at exactly 15°·5 C. (= 60° F.), for alcohol dilating rapidly by increase of temperature, very erroneous results may be obtained if this precaution be not rigidly observed.[1] Care must be taken that the bottle contains no air-bubbles, and the stopper must be inserted when the liquid in the bottle (after being well stirred) shows a temperature of 15°·5 C. (= 60° F.). A bottle holding 50 c.c. is of suitable capacity for general use, but for some purposes a smaller one will be found serviceable. It should never be trusted to contain the weight of water marked on it, but should be carefully filled with water at 15°·5 C. (= 60° F.) and the weight accurately noted. The weight of the contained spirituous liquid is then in each case divided by the observed weight of contained water, the dividend being the specific gravity of the sample. It is desirable to use a bottle having a thermometer attached to the stopper, so

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[1] If all available water be sensibly above the standard temperature, it can readily be cooled by dissolving in it some powdered thiosulphate of sodium, the specific gravity bottle filled with spirit being immersed in the cooling liquid. When the temperature of the spirit is but a few degrees above 15°·5 C., a correction of the observed density may be made according to the following formula, in which D is the required density at 15°·5 C., D′ the observed density, and *d* the difference in temperature between 15°·5 C. and that at which the experiment was made. $D = D' + d\left(\cdot 00014 + \frac{1 - D'}{150}\right)$. When the temperature of the experiment is below 15°·5 C., the fraction $d\left(\cdot 00014 + \frac{1 - D'}{150}\right)$ must be *subtracted* from D′ instead of being *added* to it.

that when the bottle is filled and the stopper inserted the thermometer will be wholly immersed in the liquid under examination, The specific gravity bottle may be conveniently replaced by the U-shaped tube described in par. 6.

155. The proportion of alcohol contained in spirituous liquids is expressed in three ways. 1. Percentage of alcohol by weight. 2. Percentage of alcohol by volume. 3. Percentage of proof spirit. Of these, the first, in the opinion of the author, is the most satisfactory, but both the other plans serve for certain purposes. It is convenient in some cases to know the weight of alcohol in 100 measures of the spirituous liquid. The term "proof spirit" has already been explained (par. 147).

156. In the following table are given the percentages of absolute alcohol by weight and of proof spirit by volume, which are contained in mixtures of alcohol and water of various densities :—

Densities of various Mixtures of Alcohol with Water.

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·79384	**100·00**	**175·25**	·819	91·36	165·18
·794	99·94	175·18	·820	·00	164·74
5	·61	174·83	1	90·64	·29
6	·29	·49	2	·29	163·84
7	98·97	·14	3	89·92	·38
8	·66	173·81	4	·54	162·88
9	·34	·47	5	·16	·38
·800	·03	·14	6	88·76	161·86
1	97·70	172·77	7	·36	·32
2	·37	·39	8	87·96	160·79
3	·03	·02	9	·58	·28
4	96·70	171·64	·830	·19	159·77
5	·37	·26	1	86·81	·26
6	·03	170·88	2	·42	158·74
7	95·68	·46	3	·04	·23
8	·32	·03	4	85·65	157·71
9	94·97	169·61	5	·27	·19
·810	·62	·20	6	84·88	156·66
1	·28	168·79	7	48	·10
2	93·92	·38	8	·08	155·55
3	·55	167·92	·8382	84·00*	155·45
4	·18	·46	·839	83·69	·02
5	92·81	·00	·840	·31	154·49
6	·44	166·53	1	82·92	153·96
7	·07	·07	2	·54	·43
8	·71	165·62	3	·15	152·89

* Rectified Spirit B.P.

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·844	81·76	152·34	·892	61·50	121·11
5	·36	151·78	3	·08	120·42
6	80·96	·21	4	60·67	119·74
7	·54	150·61	5	·26	·05
8	·13	·00	6	59·83	118·34
9	79·72	149·38	7	·39	117·61
·850	·32	148·84	8	58·95	116·88
1	78·92	·27	9	·50	·11
2	·52	147·69	·900	·05	115·32
3	·12	·11	1	57·63	114·62
4	77·71	146·51	2	·21	113·92
5	·29	145·89	3	56·77	·18
6	76·88	·28	4	·32	112·41
7	·46	144·66	5	55·86	111·64
8	·04	·04	6	·41	110·84
9	75·59	143·35	7	54·95	·03
·860	·14	142·66	8	·48	109·20
1	74·68	141·96	9	·00	108·36
2	·23	·26	·910	53 57	107·61
3	73·79	140·59	1	·13	106·86
4	·38	139·96	2	52·68	·07
5	72·96	·32	3	·23	105·27
6	·52	138·65	4	51·79	104·50
7	·09	137·98	5	·38	103·78
8	71·67	·33	6	50·96	·05
9	·25	136·69	7	·52	102·28
·870	70·84	·07	8	·09	101·51
1	·44	135·45	9	49·64	100·68
2	·04	134·84	**·91984**	**49·24***	**100·00**
3	69·63	·19	·9200	·16	99·86
4	·21	133·54	05	48·96	·49
5	68·79	132·89	10	·73	·08
6	·38	·23	15	·50	98·67
7	67·96	131 58	20	·27	·26
8	·54	130·92	25	·05	97·85
9	·13	·26	30	47·82	·44
·880	66·70	129·57	35	·59	·03
1	·26	128·87	40	·36	96·62
2	65·83	·19	45	·14	·21
3	·42	127·52	50	46·91	95·79
4	65·00	126·85	55	·68	·38
5	64·57	·15	60	·46	94·97
6	·13	125·44	65	·23	·55
7	63·70	124·73	70	·00	·14
8	·26	·02	75	45·77	93·73
9	62·82	123·29	80	·55	·31
·890	·36	122·53	85	·32	92 89
1	61·92	121·79	90	·09	·48

* Proof Spirit.

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·9295	46·86	92·06	·9540	32·25	67·92
·9300	·64	91·64	45	31·94	·30
05	·41	·23	50	·62	66·68
10	·18	90·81	55	·31	·05
15	43·95	·39	60	·00	65·43
20	·71	89·59	65	30·72	64·87
25	·48	·50	70	·44	·32
30	·24	·06	75	·17	63·77
35	·00	88·62	80	29·87	·17
40	42·76	·18	85	·53	62·49
45	·52	87·73	90	·20	61·82
50	·29	·29	95	28·87	·16
55	·05	86·84	·9600	·56	60·53
60	41·80	·37	05	·25	59·90
65	·55	85·90	10	27·93	·26
70	·30	·43	15	·57	58·53
75	·05	84·96	20	·21	57·80
80	40·80	·49	25	26·87	·09
85	·55	·02	30	·53	56·41
90	·30	83·54	35	·20	55·73
95	·05	·07	40	25·86	·03
·9400	39·80	82·59	45	·50	54·30
05	·55	·12	·9650	·14	53·56
10	·30	81·64	1	·07	·42
15	·05	·17	2	·00	·27
20	38·78	80·64	3	24·92	·11
25	·50	·11	4	·85	52·95
30	·22	79·57	5	·77	·80
35	37·94	·04	6	·69	·64
40	·67	78·50	7	·62	·48
45	·39	77·96	8	·54	·32
50	·11	·42	9	·46	·16
55	36·83	76·88	·9660	·38	·00
60	·56	·34	1	·31	51·84
65	·28	75·80	2	·23	·69
70	·00	·26	3	·15	·53
75	35·75	74·78	4	·08	·37
80	·50	·30	5	·00	·21
85	·25	73·81	6	23·92	·05
90	·00	·33	7	·85	50·89
95	34·76	72·87	8	·77	·73
·9500	·52	·41	9	·69	·57
05	·29	71·94	·9670	·62	·41
10	·05	·48	1	·54	·25
15	33·76	70·92	2	·46	·10
20	·47	·34	3	·38	49·94
25	·18	69·76	4	·31	·78
80	32·87	·16	5	·23	·63
35	·56	68·54	6	·15	·47

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° C.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·9677	23·08	49·31	·9726	19·17	41·16
8	·00	·15	7	·08	40·98
9	22·91	48·99	8	·00	·81
·9680	·85	·83	9	18·92	·64
1	·77	·67	·9730	·85	·48
2	·69	·51	1	·77	·32
3	·62	·35	2	·69	·16
4	·54	·19	3	·62	·00
5	·46	·03	4	·54	39·83
6	·38	47·87	5	·46	·67
7	·31	·71	6	·38	·51
8	·23	·55	7	·31	·35
9	·15	·39	8	·23	·19
·9690	·08	·23	9	·15	·03
1	·00	·07	·9740	·08	38·87
2	21·91	46·92	1	·00	·71
3	·85	·76	2	17·91	·53
4	·77	·59	3	·83	·36
5	·69	·43	4	·75	·18
6	·62	·27	5	·66	·01
7	·54	·11	6	·58	37·83
8	·46	45·95	7	·50	·66
9	·38	·79	8	·42	·48
·9700	·31	·63	9	·33	·31
1	·23	·47	·9750	·25	·13
2	·15	·31	1	·17	36·96
3	·08	·15	2	·08	·78
4	·00	44·99	3	·00	·61
5	20·91	·81	4	16·91	·43
6	·83	·63	5	·83	·27
7	·75	·46	6	·75	·11
8	·66	·29	7	·66	35·95
9	·58	·12	8	·58	·77
·9710	·50	43·94	9	·50	·62
1	·42	·77	·9760	·42	·46
2	·33	·60	1	·33	·30
3	·25	·42	2	·25	·14
4	·17	·25	3	·17	34·97
5	·08	·07	4	·08	·82
6	·00	42·90	5	·00	·66
7	19·91	·73	6	15·91	·50
8	·83	·55	7	·83	·32
9	·75	·38	8	·75	·14
·9720	·66	·20	9	·66	33·96
1	·58	·03	·9770	·58	·78
2	·50	41·85	1	·50	·61
3	·42	·68	2	·42	·43
4	·33	·51	3	·33	·26
5	·25	·33	4	·25	·08

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·9775	15·17	32·91	·9824	11·31	24·52
6	·08	·73	5	·23	·36
7	·00	·56	6	·15	·20
8	14·91	·38	7	·08	·04
9	·83	·18	8	·00	23·87
·9780	·75	31·99	9	10·91	·67
1	·66	·79	·9830	·81	·47
2	·58	·60	1	·72	·27
3	·50	·41	2	·63	·07
4	·42	·22	3	·54	22·87
5	·33	·03	4	·44	·67
6	·25	30·84	5	·35	·47
7	·17	·64	6	·26	·27
8	·08	·45	7	·16	·07
9	·00	·26	8	·07	21·87
·9790	13·92	·10	9	9·99	·70
1	·85	29·93	·9840	·92	·55
2	·77	·77	1	·85	·40
3	·69	·61	2	·78	·25
4	·62	·44	3	·70	·08
5	·54	·29	4	·63	20·93
6	·46	·11	5	·56	·78
7	·39	28·95	6	·49	·63
8	·31	·79	7	·41	·46
9	·23	·62	8	·34	·31
·9800	·15	·46	9	·27	·16
1	·08	·29	·9850	·20	·01
2	·00	·13	1	·12	19·84
3	12·92	27·97	2	·05	·69
4	·85	·80	3	8·98	·54
5	·77	·64	4	·91	·38
6	·69	·48	5	·84	·23
7	·62	·31	6	·77	·08
8	·54	·15	7	·70	18·93
9	·46	26·98	8	·62	·76
·9810	·39	·82	9	·55	·61
1	·31	·66	·9860	·48	·46
2	·23	·49	1	·41	·31
3	·15	·33	2	·34	·16
4	·08	·16	3	·27	·01
5	·00	·00	4	·20	17·86
6	11·92	25·83	5	·13	·71
7	·85	·66	6	·06	·56
8	·77	·50	7	7·99	·41
9	·69	·34	8	·92	·26
·9820	·62	·17	9	·85	·10
1	·54	·01	·9870	·78	16·95
2	·46	24·84	1	·71	·80
3	·39	·68	2	·64	·65

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
98·73	7·57	16·50	·9922	4·39	9·62
4	·50	·35	3	·33	·49
5	·43	·20	4	·27	·36
6	·37	·07	5	·20	·20
7	·30	15·92	6	·14	·07
8	·23	·77	7	·08	8·94
9	·16	·62	8	·02	·81
·9880	·09	·47	9	3·96	·68
1	·02	·31	·9930	·90	·55
2	6·95	·16	1	·84	·42
3	·89	·03	2	·78	·29
4	·82	14·88	3	·73	·18
5	·75	·73	4	·67	·05
6	·69	·60	5	·61	7·92
7	·62	·45	6	·55	·79
8	·55	·30	7	·49	·66
9	·49	·17	8	·43	·53
·9890	·42	·02	9	·37	·40
1	·35	13·87	·9940	·32	·29
2	·29	·74	1	·26	·16
3	·22	·59	2	·20	·02
4	·15	·43	3	·14	6·89
5	·09	·30	4	·08	·76
6	·02	·15	5	·02	·63
7	5·96	·02	6	2·97	·52
8	·85	12·87	7	·91	·39
9	·83	·74	8	·85	·26
·9900	·77	·61	9	·79	·13
1	·70	·46	·9950	·74	·02
2	·64	·33	1	·68	5·89
3	·58	·20	2	·62	·76
4	·51	·05	3	·57	·65
5	·45	11·92	4	·51	·52
6	·39	·79	5	·45	·39
7	·32	·64	6	·39	·25
8	·26	·51	7	·34	·14
9	·20	·38	8	·28	·01
·9910	·13	·22	9	·22	4·88
1	·07	·09	·9960	·17	·77
2	·01	10·96	1	·11	·64
3	4·94	·81	2	·05	·51
4	·88	·68	3	1·99	·38
5	·82	·55	4	·94	·27
6	·76	·42	5	·89	·16
7	·70	·29	6	·83	·03
8	·64	·16	7	·78	3·92
9	·57	·01	8	·73	·81
·9920	·51	9·88	9	·67	·68
1	·45	·75	·9970	·61	·54

Densities of various Mixtures of Alcohol with Water—*continued.*

Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15°·5 C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·9971	1·56	3·43	·9986	0·74	1·63
2	·51	·32	7	·69	·52
3	·45	·19	8	·64	·41
4	·40	·08	9	·58	·28
5	·34	2·95	·9990	·53	·17
6	·29	·84	1	·47	·04
7	·23	·71	2	·42	0·93
8	·18	·60	3	·37	·82
9	·12	·47	4	·32	·71
·9980	·07	·36	5	·26	·57
1	·02	·25	6	·21	·46
2	0·96	·12	7	·16	·35
3	·91	·01	8	·11	·24
4	·85	1·87	9	·05	·11
5	·80	·76	1·0000	·00	·00

157. In the part of the foregoing table referring to alcohol of greater strength than proof spirit, only the percentages of alcohol and proof spirit are given which correspond to densities which can be accurately expressed by three figures. Between the concentrations of 49 and 25 per cent. of absolute alcohol the table is more extended, and for still more dilute spirit the percentages of alcohol and proof spirit are given which correspond to every degree of density expressed to the fourth place of decimals. As arranged, the table will be found sufficiently copious for all cases likely to occur in practice. When it is desired to ascertain, in strong spirit, the proportion of alcohol corresponding to a determination of density to the fourth decimal place, it may be effected by intercalation. The following example shows the application of the method to a sample of spirit of ·8673 specific gravity:—$72{\cdot}09 - 71{\cdot}67 = {\cdot}42$; and $\frac{{\cdot}42 \times 3}{10} = {\cdot}126$; and $72{\cdot}09 - {\cdot}126 = 71{\cdot}964$, as the percentage of alcohol in spirit of a density of ·8673.

158. The following rules give the means of calculating percentages of alcohol by weight or volume to the corresponding percentages of proof spirit, and *vice versa.* The percentage of alcohol by volume is a mode of expression not common in England, but is the usual way of valuing spirit adopted in France, Belgium, Germany, the United States, and some other countries.

a. The percentage by *volume of absolute alcohol* may be obtained by multiplying the percentage of proof spirit by the factor 0·5706.

b. The percentage by *volume of absolute alcohol* may also be obtained by multiplying the percentage of alcohol by weight by the observed specific gravity, and dividing the product by 0·7938 (or multiplying it by 1·26).

c. The percentage by *volume of proof spirit* can be obtained by dividing the percentage of absolute alcohol by volume by 0·5706 (or multiplying it by 1·7525).

d. The percentage by *volume of proof spirit* may be obtained by multiplying the percentage by weight of absolute alcohol by the specific gravity, and the product by 2·208.

e. The percentage of *absolute alcohol by weight* may be found by dividing the percentage of proof spirit by the product of the specific gravity and 2·208.

f. The percentage of *absolute alcohol by weight* may be found by multiplying the percentage of alcohol by volume by 0·7938, and dividing the product by the density.

If the percentage of alcohol by weight be called W, the percentage by volume V, the percentage of proof spirit P, and the specific gravity D, then the following equations embody the instructions given in the foregoing rules :—

$$a.\ V = P \times 0{\cdot}5706.$$

$$b.\ V = \frac{WD}{0{\cdot}7938} = WD \times 1{\cdot}26.$$

$$c.\ P = \frac{V}{0{\cdot}5706} = V \times 1{\cdot}7525.$$

$$d.\ P = WD \times 2{\cdot}208.$$

$$e.\ W = \frac{P}{D \times 2{\cdot}208}.$$

$$f.\ W = \frac{V \times 0{\cdot}7938}{D}.$$

159. When it is required to calculate the proportion of proof or any other strength of spirit a particular sample of alcohol contains, or would contain, when diluted, the following formula should be used:—

$$\frac{\text{Percentage of proof spirit in alcohol required} \times 100}{\text{Percentage of proof spirit in sample}} = \left\{\begin{array}{l}\text{The number of volumes of the stronger}\\ \text{spirit which will produce or be con-}\\ \text{tained in 100 measures of the more}\\ \text{dilute spirit.}\end{array}\right.$$

Thus, if it be required to know what percentage of gin at 20° U.P. is contained in a watered sample of 44° U.P., the following calculation will suffice :—

$\frac{56 \times 100}{80} = 70$ per cent. by volume. Hence the sample is of a strength corresponding to the dilution of 7 gallons of gin at 20° U.P. to 10 gallons by addition of water.

Again, to ascertain the proportion of water which must be added to spirit at 35° O.P., to reduce the strength to 10° U.P. :— $\frac{90 \times 100}{135} = 66{\cdot}7$. That is to obtain spirit of 10° U.P. 66·7 measures of spirit at 35° O.P. must be diluted to 100, or every two gallons must be made up to three by addition of water.

160. A colorimetric method of determining alcohol has been described by M. Monell (*Chem. Centr.*, 1877, 24). It is based on the fact that the addition of nitrate of cobalt to an alcoholic solution of ammonium thiocyanate (sulphocyanide) produces a deep blue colour which disappears on dilution with water, and is restored by a furthur addition of alcohol. If a measured quantity of this deep blue liquid be poured into a cylinder and the liquid to be tested be added till a certain standard tint is reached, the volume of the mixed liquids will be greater the more alcohol the sample contains. The standard tint may be obtained by the use of a sample containing a known proportion of alcohol, and if it be made the same as a piece of cobalt-blue glass the latter may be substituted for it in subsequent experiments. The blue solution of cobalt thiocyanate must always be prepared with alcohol of the same strength. The author of this process states that it will give results within $\frac{1}{4}$ per cent. of the truth. A. Vogel writes favourably of the method, and "believes it might be developed so as to give approximate results."

Other plans for the determination of alcohol have been based on its rate of dilatation by heat, on the surface-tension of the liquid, on the tension of its vapour, and on its boiling point. These methods are capable of being used with advantage under special circumstances, but they require special apparatus and are generally less accurate and convenient than those already given. For the general purposes of the laboratory the determination of alcohol by observation of its density is by far the best plan.

161. *For the determination of very small quantities of alcohol*, the following method described by A. Dupré (*Jour. Chem. Soc.*, xx. 495) may be very advantageously used. It was first proposed by E. Chapman, and is based on the fact that when alcohol is heated with chromic acid it is oxidised to acetic acid, which may be distilled off and titrated with accuracy by standard alkali.[1]

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[1] According to L. Danesi, acetic acid is oxidised by hot chromic acid or potassium bichromate and sulphuric acid, with formation of carbonic acid. It is probable that any such action is strictly confined to very concentrated liquids. On the other hand, the formic acid produced from methyl alcohol is urther oxidised with great facility.

In practice, a weighed amount of spirituous liquid is taken which will contain about 0·1 gramme (not more than 0·2) of real alcohol.[1] This is made up to about 20 c.c. by addition of water, and is placed in a small strong flask. A liquid is next prepared containing 10 grammes of potassium bichromate and 20 grammes (or 11·8 c.c.) of strong sulphuric acid in each 100 c.c., the volume being made up with water.[2] 10 c.c. of this chromic acid solution are introduced into the flask, which is then securely closed by an india-rubber stopper tied down, and suspended in a bath of boiling water for two hours, by which time all the alcohol will have been oxidised to acetic acid. After cooling, the flask is opened and sulphuric acid and granulated zinc added to reduce the excess of chromic acid. The green liquid is then distilled, pumice or tobacco-pipe being added to prevent bumping. When nearly dry, water should be added and the distillation repeated. The acetic acid in the distillate is then determined by titration with decinormal soda, and phenolphthaleïn as indicator. Before commencing the titration it is desirable to add a drop or two of barium chloride as a test for sulphuric acid. Any precipitate must be filtered off, and 46 parts of alcohol subtracted for every 233 of barium sulphate obtained. Each 1 c.c. of decinormal alkali required represents 0·0046 gramme of real alcohol in the liquid examined. In presence of acetic acid or foreign fixed matter, the spirituous liquid must be rendered slightly alkaline and distilled,[3] the chromic acid treatment being applied to the distillate or a portion of it.

The method of Thresh, described in par. 151, *d*, may be employed for the approximate determination of small quantities of alcohol.

162. **The Determination of Alcohol in presence of fixed matters** cannot be effected directly by the specific gravity method, but approximate results can be obtained by several of the alternative processes already given. The indirect determination by the density may be effected in wine and beer with tolerable accuracy by the following method devised by Tabarie :—

a. The specific gravity of the original liquid is first accurately observed. A measured quantity, such as 100 c.c., is then boiled sufficiently long to volatilise all the alcohol, and the "extract" subsequently made up with water again to the exact original

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[1] Larger quantities may be used if the proportions of water and oxidising mixture are duly increased.

[2] These proportions are sufficient for the reaction—

$$K_2Cr_2O_7 + 5H_2SO_4 = Cr_2(SO_4)_3 + 2KHSO_4 + 4H_2O + O_3.$$

[3] A further concentration of the alcohol by redistillation from a slightly acid liquid is often desirable.

bulk, the dilution being executed at 15°·5 C. (=60° F.). Then,

$$\frac{\text{Specific gravity of original liquid}}{\text{Specific gravity of the ``extract''}}=\text{Specific gravity of the alcohol evaporated.}$$

From the last figure the proportion of alcohol can be ascertained by reference to the table in par 156. When beer or wine is examined by this method, the estimation of alcohol has a tendency to be low, but the process is extremely simple and the results approximate closely to the truth.

163. *b.* The following method for the determination of alcohol in wine and other alcoholic liquids containing fixed matters is of very general application and is thoroughly satisfactory :—

50 c.c. of the sample are accurately measured at 15°·5 C. (=60° F.). In the case of beer and other liquids weak in spirit, 100 c.c. may be appropriately taken. Any free acid in the sample is next neutralised by a cautious addition of caustic soda, which should be used in amount sufficient to impart a slight alkaline reaction. About 0·1 gramme of tannin is next added (to prevent frothing), and the liquid is made up with water to about 150 c.c.

It is next placed in a small retort or flask fitted air-tight to a Liebig's condenser, or similar arrangement allowing of thorough cooling of the vapours, and is distilled by a gentle heat, the distillate being collected in a flask holding 100 c.c. When the distillate has a volume within a few centimetres of this quantity, the operation is arrested, the distillate thoroughly mixed by agitation, and brought to a temperature of 60° F., when it is made up to 100 c.c. exactly by addition of distilled water at 60° F. The liquid is again well mixed, and the density carefully taken by a 50 c.c. specific gravity bottle, or a Sprengel's tube, when a reference to the table (par. 156) will at once show the percentage of alcohol by weight contained in the distillate. Then,

$$\frac{\text{Density of distillate}\times\text{measure of distillate in c.c.}\times\text{per cent. of alcohol found in distillate by table}}{\text{Density of sample}\times\text{measure of sample taken in c.c.}}$$
$$=\text{Percentage of absolute alcohol by weight contained in } \textit{the sample.}$$

This calculation involves the necessity of knowing the *density* of the *original sample.* If unknown, the determination may be avoided by carefully weighing the 50 or 100 c.c. taken for the experiment, and substituting this weight in grammes for the denominator of the above fraction.

The calculation can be wholly avoided, and a more satisfactory result obtained by *weighing* the original sample instead of measuring it, and also weighing the distillate. About 50 grammes of the sample should be taken, and the distillate may conveniently be made up to about 100 c.c., and weighed. After thoroughly mixing the liquid its density is taken, when,

$$\frac{\text{Weight of distillate} \times \text{percentage of alcohol found in distillate by table}}{\text{Weight of sample taken}}$$
$$= \text{Percentage of absolute alcohol by weight contained in } \textit{the sample.}$$

In the case of strong spirituous liquids, the sample may be advantageously diluted to four times (instead of three times) its original bulk before commencing the distillation, the boiling being continued till three-fourths (instead of two-thirds) of the entire liquid has passed over.

In the case of very weak alcoholic liquids, a second distillation from a faintly acid liquid is often desirable.

To avoid loss of alcohol by imperfect condensation, it is desirable, when small quantities are to be determined, or very accurate results are required, to use an apparatus in which the retort and receiver are both connected air-tight with the condenser. A suitable receiver for the purpose is a small cylinder graduated at 50, 100, and 150 c.c., and furnished with an india-rubber stopper pierced with two holes, through one of which passes the end of the condenser tube, while the other carries a safety-tube, or funnel, closed by mercury. By operating in this manner, a certain contraction and expansion of the contained air is permitted, while all loss is prevented. When the amount of the distillate approaches the desired volume, the receiver is detached, and the contained liquid transferred to a flask or suitable vessel for weighing or measuring, the volume being made up with the rinsings of the receiver.

164. Distillation from a neutralised liquid suffices to *separate alcohol* from fixed substances like sugar and salt, from acids (*e.g.*, acetic), and from bodies of high boiling point, such as glycerin. In presence of ether, chloroform, and other readily volatile bodies, the distillate will contain these, and must be subsequently examined by special methods adapted for the particular case in question. From compound ethers generally, alcohol is best separated by treating the distillate with twice its measure of a saturated aqueous solution of calcium chloride, in which most of the ethers are insoluble. In other cases the separation may be effected by adding anhydrous calcium chloride, with which any water and alcohol combine, while the ethers may be distilled off by the heat of a water-bath. By subsequently adding water, the alcoholic compound with chloride of calcium is decomposed, and the alcohol may be obtained by distillation. Fractional distillation may be

conveniently employed in some cases. Any determination of the alcohol in such mixtures will generally be merely approximate, though in special cases fairly good results are obtainable. (See articles on ether, compound ethers, chloroform, methyl alcohol, amyl alcohol, tinctures, &c.)

Appendix to Ethyl Alcohol.

ALCOHOLIC AND FERMENTED LIQUORS.

165. **Fermented liquors** are those produced by allowing the propagation in a saccharine liquid of a peculiar, low vegetable growth, which feeds on the sugar, and converts it into the excretary products **alcohol** and **carbon dioxide**, together with smaller quantities of other bodies.

166. Although alcohol may be synthetically produced by a variety of laboratory processes, the fermentation of saccharine matter is the method always resorted to on a large scale. Sugar exists ready formed in the grape, but when alcohol is produced from grain the starch of the seed is first converted into sugar, and this is subsequently changed to alcohol.

167. Although various kinds of sugar can be used for the production of alcohol, the glucoses only appear to be capable of direct alcoholic fermentation, other kinds of sugar undergoing a previous conversion into glucose. Thus, when an aqueous solution of cane sugar is mixed with yeast, and exposed to a temperature of about 30° C., the sucrose is converted into the mixture of glucoses known as "invert sugar,"[1] the density of the liquid increases, and the glucoses subsequently ferment, with production of **alcohol** and **carbon dioxide**, according to the equations:—

$$\underset{\text{Cane Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Invert Sugar.}}{2C_6H_{12}O_6}; \text{ and}$$

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_6O_2} + \underset{\text{Carbon Dioxide.}}{2CO_2}.$$

168. The change of the starch of grain, malt, or potatoes into the variety of sugar called maltose is effected by a peculiar nitrogenised ferment called **diastase**, the proportion of which in malt is said not to exceed ·002 or ·003 per cent. of its weight. Subsequently, under the action of the yeast-ferment (*Saccharomyces*

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[1] If the proportion of yeast be very small, the change never goes beyond the formation of invert sugar, the formation of which is due to the action of a soluble ferment called *invertin*.

cerevisiæ), the maltose is converted into glucose, which splits up into alcohol and carbon dioxide.

In the case of the fermentation of grape-juice, the change of the glucose into alcohol is brought about by a ferment existing on the skins of the fruit.

In all cases the production of alcohol is accompanied by evolution of gas and "attenuation" or decrease in the specific gravity of the liquid. According to the nature of the liquid and the management of the process, the product is wine, beer, cider, koumiss, &c. By distillation, the alcohol can be separated from the fixed matters, and is then known as cognac, whisky, rum, &c., according to its origin.

169. Ethyl alcohol and carbonic acid are the chief, but by no means the sole products of vinous fermentation. The higher homologues of ethylic alcohol are probably always produced in greater or less proportion, and Pasteur has shown that glycerol (glycerin), $C_3H_8O_3$, and succinic acid are constant products of the vinous fermentation. The proportion of succinic acid formed varies from 0·6 to 0·9 per cent. of the weight of the cane sugar fermented, and the glycerin from 3·2 to 3·7 per cent. Thus, 100 grammes of sugar-candy, fermented with 1·198 grammes of dry yeast, gave 0·673 grammes of succinic acid and 3·640 grammes of glycerin, or a total of 4·130 grammes.[1] In consequence of the constant formation of these, and traces of other products, the proportion of alcohol produced is not 54·97 per cent. of the weight of the cane sugar taken, as would be the case if the above formula were rigidly correct, but only 51 per cent., or 51½ per cent. at the outside.

As a secondary product of the alcoholic fermentation, there is also in practice a constant production of acetic acid, which is generally considered to originate from the yeast itself, in which there is present more or less of the *acetic* ferment, *mycoderma aceti*.

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[1] The method employed by Pasteur for determining the succinic acid and glycerin in the fermented liquid was as follows :—When the fermentation was over and all the sugar had disappeared (which occurred in fifteen to twenty days, under favourable conditions), the liquid was filtered and evaporated very slowly, so that from twelve to twenty hours were required for each 500 c.c. When the liquid was reduced in bulk to 10 or 20 c.c., the evaporation was continued *in vacuo* over sulphuric acid. The syrup obtained was then treated with a mixture of two measures of strong alcohol with three of ether, and the liquid filtered. The ether-alcohol, containing the succinic acid and glycerin, was concentrated in a water-bath, and the residue dried again in a vacuum. The residue was treated with lime water in slight excess, the liquid again evaporated, and the glycerin dissolved out from the calcium succinate by ether-alcohol. The solution, on evaporation in a dry vacuum, left the glycerin in a condition fit for weighing, while the calcium succinate was purified by treatment with 80 per cent. spirit, dried and weighed.

170. The abnormal fermentation of liquids, by which they become sour, ropy, or putrid, is in each case produced by a particular ferment. Thus the *lactic* acid ferment (*Penicillium glaucum*) decomposes sugar into lactic acid, $C_3H_6O_3$; the *butyric* acid ferment attacks fatty matters with liberation of butyric acid $C_4H_8O_2$; and *putrid ferments*, owing to their avidity for oxygen, split up complex organic matters into a variety of simpler products. Under certain conditions, cane sugar is apt to undergo the *mucous* fermentation, by which it is converted into mannite, $C_6H_{14}O_6$, gum, $C_6H_{10}O_5$, and carbon dioxide, the average production being 51 per cent. of mannite and 45½ per cent. of gum. Beet-root juice and certain white wines are especially apt to undergo the mucous fermentation.

171. The action of yeast cells on sugar is prevented by too great concentration of the solution, whether due to alkaline chlorides, gelatin, glycerin, or sugar itself. The presence of strong mineral acids, even in small proportion, prevents or retards the vinous fermentation, phosphoric acid alone acting favourably. Fermentation is also prevented by a very small quantity of carbolic, salicylic, or sulphurous acid, or other antiseptic; or by a considerable proportion of alcohol.

172. The following table shows the percentage of absolute alcohol present in certain typical fermented liquors, as they occur in commerce. In the case of the stronger wines, an *addition* of alcohol has been made.

Port (old bottled), ...	20·2	Rüdesheimer, ...	9·2
„ (newly bottled), . .	17·4	Auerbacher, ...	8·4
Sherry (Montilla, 1854), . .	16·3	Burton ale, ...	5·9
Fine Marsala, ...	17·0	Edinburgh ale, . .	5·7 to 6·1
Madeira, ...	16·1	London porter, . .	5·4 to 6·9
Beaune, ...	13·5	Munich lager-bier, . . .	5·1
Champagne, ...	10·0	Cider, ...	4·6
Château-Lafitte, ...	8·7	Schenkbier, ...	3·8
Bordeaux (ordinary), .	6·4 to 8·7	Berlin Weissbier, . .	1·8 to 2·0

173. The Proportion of Alcohol in fermented liquors cannot be deduced by a direct determination of the density, though very fair results are obtainable by Tabarie's indirect method (par. 163, *a*), especially if the sample be neutralised by agitation with magnesia and filtered before ascertaining the density of the alcoholic liquid. A greater degree of accuracy is attainable by the distillation-method (par. 163, *b*). In the case of wine, the determination of alcohol by

distillation is apt to be slightly in excess of the truth, owing to the presence of volatile ethers in the distillate, while the results by Tabarie's method are correspondingly low. Hence Löwe recommends that, where great accuracy is required, both methods should be employed, and the mean of the two results regarded as the truth.

174. **Wine.**—*French,* Vin. *German,* Wein.

Strictly defined, wine is the pure fermented juice of the grape. In practice, pure wine may have received certain additions essential to the stability or keeping of the liquid. The following is a comparative statement of the usual constituents of "must" or grape juice, and the wine resulting from its fermentation:—

MUST.	WINE.
Water, 73 to 86 %.	Water.
Albuminoid matters.	Residues of albuminoid matters.
Glucose (chiefly dextrose), 12 to 24 %.	Glucose (chiefly lævulose). Alcohol, 6 to 13 %. Glycerin, 0·5 to 1·5 %. Succinic acid. Acetic acid. Ethers.
Gum.	Gum.
Vegetable mucus.	
Colouring matters (traces only).	Colouring matters.
Tannin (traces).	Tannin.
Malic acid (in bad seasons).	Malic acid (in bad seasons).
Potassium hydrogen tartrate. Calcium tartrate.	Tartaric acid. Potassium hydrogen tartrate. Calcium tartrate.
Other salts of organic acids.	Other salts of organic acids.
Mineral matters.[1]	Mineral matters.
Specific gravity, 1065 to 1107.	Specific gravity, 991 to 996.
Total dry residue, 14 to 27 %.	Total dry residue, 1 to 3 %.

175. J. Carter Bell (*Analyst*, v. 41; vi. 197, 221) obtained the

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[1] The following is the average *composition of the ash* of genuine grape juice, as deduced from analyses by J. Carter Bell (*Analyst*, vi. 197) of eighteen representative samples :—

K_2O	Na_2O	CaO	MgO	Fe_2O_3 & Al_2O_3	SiO_2	P_2O_5	SO_3	Cl
42·14	3·37	11·48	9·67	0·75	0·29	9·60	9·14	1·09

The potash varied from 54·24 to 31·23 per cent., and the sulphuric anhydride from 13·68 to 3·14 per cent. The total ash ranged from 0·26 to 0·39 per cent. of the grape juice. From 56·6 to 90·6 per cent. of the total ash was soluble in water.

following results by the analysis of the juice of two species of grape.[1] The figures are grammes for 100 c.c.

	Black English Grapes.	White Almeira Grapes.
Specific gravity, . . .	1083·5	1071·0
Extract, dried at 100° C., . .	22·90	20·28
„ „ 110° C., . .	18·61	15·96
Glucose, ...	13·21	12·60
Free acid, calculated as tartaric,	·70	·60
Ash, total, ...	·356	·331
„ soluble in water, . . .	·322=90·56 %	·296–89·42 %

176. In completely fermented wines the glucose is almost wholly converted into alcohol, and hence Burgundy, Moselle, Rhenish, Carlowitz, and Claret contain little or no sugar. Sweet wines, such as port and sherry, contain a notable quantity of unfermented sugar. A "dry" wine will contain less sugar than a "full-bodied" wine. To prevent the sugar from undergoing subsequent fermentation, sweet wines require to be fortified by an addition of brandy. Cane sugar is added to the must of the champagne grape before fermentation, to give it body and keep it sparkling and free from acetification. Only the very purest cane sugar is suitable for this purpose.[2] In wines which have been "plastered" by adding gypseous earth to the grapes or must, the potassium hydrogen tartrate is largely converted into potassium sulphate and free tartaric acid.

By long keeping, the colouring matters and acid tartrate of potassium are in great measure deposited ("crust," "bees' wing"), while the free acids are partially converted into ethyl acetate, tartrate, &c. These and traces of other ethers give to old wine the delicate flavour and "bouquet" so highly prized by connoisseurs.

177. The following figures by Dupré show the leading constituents of high priced wines of which the fermentation has been arrested by addition of alcohol. The figures are grammes per 100 c.c.

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[1] These and various other analyses of genuine grape-juice were made by J. C. Bell for comparison with various samples of fictitious "unfermented wine," patronised by total abstainers and stated to be "manufactured from the juice of the grape, for family and sacramental use," but which were really composed of solutions of sugar and tartaric acid, flavoured and coloured, with an addition of salicylic acid to prevent fermentation.

[2] However good in quality white sugar obtained from beet-root may be, on fermentation it always produces an alcoholic liquid having a disagreeable taste. Hence the white sugar employed in the manufacture of champagne ought always to be derived from the sugar-cane.

	Sherry (1860).	Madeira (E. Indian).	Marsala (old).	Port (1854).	Port (1842).
Specific gravity, . .	997·9	993·9	996·6	997·4	986·9
Alcohol, ...	17·20	17·75	16·71	17·53	18·26
Extract, ...	5·35	4·35	4·98	5·39	3·10
Glucose, ...	2·97	2·08	3·24	2·28	1·01
Mineral matters, . .	0·55	0·39	0·22	0·26	0·21
Acidity (as H_2T), . .	0·52	0·54	0·33	0·49	0·40
Phosphoric acid, . .	0·025	0·042	0·018	0·033	0·033

The proportion of alcohol in fortified wines is sometimes as high as 22 per cent., but in natural wines it never exceeds 13 per cent.

The following results by Fresenius and Borgmann (*Zeit. Anal. Chem.*, xxii. 46) show the average composition of certain pure wines, in grammes for 100 c.c.[1]:—

	Red Main.	White Main.	Hocks.	White French.	Red French.	Moselle.
Alcohol { Maximum, . . .	9·51	10·15	10·39	9·84	9·32	8·72
Alcohol { Minimum, . . .	9·49	8·90	6·42	9·05	7·99	7·04
Alcohol { Average, . . .	9·50	9·52	8·77	9·44	8·56	8·08
Extract, ...	3·00	2·43	2·32	2·54	2·44	2·11
Mineral matters, . . .	0·32	0·19	0·22	0·26	0·25	0·18
Acidity, ...	0·58	0·69	0·66	0·62	0·54	0·79
Glycerin, ...	1·19	1·10	0·92	0·94	0·86	0·73
Sulphuric acid (SO_3), . .	0·076	0·044	0·047	0·017	0·013	0·012
Phosphoric acid (P_2O_5), . .	0·065	0·039	0·040	0·034	0·027	0·047

The solid matters ranged from 3·30 to 1·86; the ash from 0·35 to 0·15; the acidity from 1·01 to 0·48; the glycerin from 1·34 to 0·64; the sulphuric acid from 0·082 to 0·006; and the phosphoric acid from 0·065 to 0·023 grammes per 100 c.c. of wine. The average mutual relations of the various constituents of the wines were as follows:—

Alcohol : glycerin = 100 : 10·5
Extract : acidity = 1000 : 16·6
Acidity : ash = 10 : 3·4
Ash : extractives = 1 : 11·2; and
Phosphoric acid : ash = 1 : 6·8.

From a number of experiments, Borgmann concludes that the proportion of glycerin to alcohol in pure wines is never less than 7·8 : 100.

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[1] Buchner (*Dingl. Polyt. Jour.*, ccxxvi. 531; *Jour. Chem. Soc.*, xxxiv. 345) has published analyses of various inferior wines.

Chemical Analysis of Wine.[1]

178. The *alcohol* in wine can be determined as indicated in par. 173.

179. *The extract* or proportion of *solid matter* may be approximately ascertained by evaporating the wine to one-fourth, and then diluting to exactly the original volume. The density of the de-alcoholised liquid is then observed at 15° C.,[2] and the number expressing it *minus* 1000, divided by 4·6, gives the grammes of solids per 100 c.c. of the wine. Thus, if, after evaporating off the alcohol, a wine be found to have a density of 1011·5 it will contain 2·50 grammes of solid matter per 100 c.c. ; for

$$\frac{1011{\cdot}5-1000}{4{\cdot}6}=2{\cdot}50\,.$$

Another method of calculating the total solids, which is preferable in the case of very sweet wines, is to divide the difference between the density and 1000 by 3·86 instead of 4·6, and subtract the percentage of ash from the figure so obtained. This method is based on the assumption that the organic solids of wine have the same solution-density as extract of malt, and that the mineral matters have twice that solution-density.

180. The direct determination of the *extract* or proportion of solid matters in wine presents some difficulty. Some operators consider the glycerin to be a proper part of the extractive matters, and hence employ processes which are intended to avoid its loss by volatilisation, while others pursue an exactly opposite system. Thus, by adding to the wine a slight excess of baryta water the volatile acids are fixed, and the evaporation of glycerin completely prevented. Nessler and Barth (*Zeit. Anal. Chem.*, xxi. 43) recommend that 50 c.c. of wine should be evaporated on a water-bath to the consistence of syrup, and the residue dried at 100° C. for three hours. After that time the weight is practically constant, continuous small losses being due to volatilisation of glycerin. If 1 per cent. of glycerin be present in the wine, about 0·14 per cent. is lost during the drying, while the loss is smaller when less glycerin is present.

181. To estimate the *glycerin* in wine, 100 c.c. of the sample should be evaporated to one-third in a porcelain dish, slaked lime

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[1] A method for the systematic analysis of wine is described in the *Jour. Soc. Chem. Industry*, ii. 136.

[2] The specific gravity of the extract diminishes by 0·24 (water = 1000) for each increase of 1° C. in the temperature.

added till the liquid is slightly alkaline, and the evaporation completed. The residue is boiled with rectified spirit, which dissolves the glycerin and leaves the succinic acid and sugar as insoluble lime compounds. The alcoholic solution, when filtered and evaporated cautiously, leaves the glycerin in a moderately pure state. In wines adulterated with starch-sugar, and in other cases if accurate results are required, the glycerin obtained as above should be dissolved in absolute alcohol, and the filtered solution treated with 1½ measures of ether. Certain impurities are precipitated by this menstruum, and the filtered solution on evaporation leaves the glycerin in a state of tolerable purity. Neubauer and Borgmann (*Zeits. Anal. Chem.*, 1878, 442; and *Jour. Chem. Soc* xxxvi. 404) find the foregoing method very satisfactory. Pure Rhenish and French wines tested by it show a proportion of glycerin ranging from 0·7 to 1·3 per cent.,[1] and as the ratio of alcohol to glycerin in genuine wine is tolerably constant (par. 177), the method sometimes serves for the detection of added alcohol or glycerin, or the recognition of the sample as factitious.

182. The *sugar* in genuine wine is wholly glucose. As dextrose is more readily fermentable than lævulose, the residual unfermented sugar of genuine wine is usually lævo-rotatory. Perfectly fermented wine is optically neutral or very feebly dextro-rotatory. On the other hand, wines prepared with starch-sugar contain considerable quantities of certain dextro-rotatory, non-fermentable bodies, which differ from those present in genuine wine by being soluble in strong alcohol. To estimate these bodies, Nessler and Barth evaporate 210 c.c. of the wine to one-fifth, after adding a few drops of a concentrated solution of potassium acetate. Rectified spirit is then added as long as a precipitate is produced, when the liquid is filtered. The filtrate is evaporated to about 15 c.c., after adding some water and purified animal charcoal, when it is again filtered, made up to 30 c.c., and examined in a 2-decimeter tube to determine its optical activity. If the solution show a greater dextro-rotation than corresponds to 0·6 sugar-units, the presence of starch-sugar is certain. In presence of unfermented sugar, an appropriate correction must be made, after estimating the sugar by known means. This is best done by Fehling's solution, after boiling off the alcohol and removing colouring and other foreign reducing matters by basic lead acetate, in the manner described in the section on "Sugars." 100 c.c. of light wines or 25 c.c. of sweet wines, treated appropriately and diluted to 200 c.c., will give solutions of suitable strength for the copper test.

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[1] The wines of the more northern vineyards of Germany show a sensibly lower proportion of glycerin.

183. *Cane Sugar* is a legitimate addition to champagne (par. 176), but it readily undergoes inversion on keeping, and hence will rarely be detected in its unaltered state. Its presence may be recognised by the dextro-rotation of the wine, changed to lævo-rotation by inversion, with corresponding increase in the cupric oxide reducing power of the sample. C. Cameron found unaltered cane sugar in low-class factitious wines.

184. The *Acidity* of genuine wine is chiefly due to the acid tartrate of potassium, though succinic acid is also a constant constituent, and free acetic and other acids are also present, especially if the wine has been exposed to the air. The free acids of wine may be conveniently classed as volatile and non-volatile, the former of which consist chiefly of acetic acid and traces of its homologues. About one-fourth of the total acidity of white wines should be due to volatile acids, and in red wines the proportion should exceed one-third of the total acidity.

185. The acidity of wines may be determined by titration with decinormal soda. 100 c.c. of the wine should be employed, and neutral litmus paper used to indicate the end of the reaction. On evaporating an equal measure of the sample to dryness, adding water, and again titrating, the acidity due to the fixed acids will be ascertained, and the difference between this result and the total acidity will be that due to the volatile acids. By distilling the wine to dryness in a vacuum, adding water, redistilling, and repeating this operation twice, the whole of the volatile acids may be collected, and examined in the manner described in the section on the "Homologues of Acetic Acid." The proportion of volatile acid in wine is usually expressed in terms of acetic acid, and the non-volatile acid as tartaric acid.

186. *Free Tartaric Acid* in factitious wines may be detected, according to J. Nessler, by shaking the liquid with powdered cream of tartar for some time, filtering, and dividing the filtrate into two portions. One of these is kept for comparison, and to the other is added a few drops of a concentrated solution of potassium acetate. On stirring the liquid and allowing it to stand, crystals of acid tartrate of potassium are deposited if the liquid contained free tartaric acid. Care must be taken to prevent any change in the temperature of the filtered liquid. In a sample of wine previously evaporated to half its volume, Nessler detected 0·05 per cent. of free tartaric acid by this process. In twenty-five out of thirty samples of artificial wine, free tartaric acid was detected without resorting to evaporation (*Zeits. Anal. Chem.*, 1879, 230).

187. A simple method of detecting free tartaric acid in wine is to neutralise 50 c.c. with caustic potash, add another 50 c.c. of the

sample, stir well, and allow the liquid to stand. The precipitate of tartar formed represents the free tartaric acid of the sample.

188. Nessler and Barth (*Zeits. Anal. Chem.*, 1882, 43) estimate potassium tartrate and free tartaric acid in wine by evaporating 100 c.c. of the sample to a thin syrup, and, while stirring constantly, adding 70 c.c. of strong alcohol. After standing four hours the precipitated tartar is filtered off, and may be washed, purified, and estimated by weight or by titration with standard alkali (see article on Tartaric Acid). To the filtrate, about 2 c.c. of a 20 per cent. solution of calcium acetate is added. In the absence of free tartaric acid the liquid remains clear. With 0·01 per cent. there is a plain reaction, and with 0·05 per cent. a distinct crystalline crust of calcium tartrate is produced within two hours.

Pure wine may contain traces of tartaric acid, but never more than 0·05 per cent. Plastering increases the free acid, and factitious wines may contain all the tartaric acid in the free state.

189. For the determination of the total tartaric and other *non-volatile organic acids* in wine, Schmitt and Hiepe (*Zeits. Anal. Chem.*, xxi. 534) employ the following process:—200 c.c. of the wine is concentrated to one-half, and basic acetate of lead added till the reaction is alkaline. The precipitate is filtered off, washed with cold water, suspended in 200 c.c. of warm water, and decomposed by sulphuretted hydrogen. The liquid is filtered while still warm, concentrated to 50 c.c., exactly neutralised by caustic potash, and again concentrated to 50 c.c. Excess of a saturated solution of calcium acetate is then added, and, after standing four or five hours with frequent stirring, the precipitate is separated, washed with cold water until the filtrate measures 100 c.c., ignited, and the ash titrated with standard acid. Each 1 c.c. of normal acid used represents 0·0750 gramme of tartaric acid in the precipitated calcium tartrate, and to the weight so obtained should be added 0·0286 gramme for loss by solubility. The filtrate from the calcium tartrate precipitate is concentrated to 20–30 c.c., and three times its measure of very strong alcohol added. The precipitate is filtered after some hours, dried at 100°, and weighed. It is then treated with hot water and sufficient hydrochloric acid to effect solution, the hot liquid filtered, and potassium carbonate added till the reaction is alkaline. The calcium carbonate is filtered off, the filtrate neutralised with acetic acid, evaporated to a low bulk, and treated boiling hot with chloride of barium. The precipitate of barium succinate and sulphate is filtered off and treated on the filter with hydrochloric acid, the residual barium *sulphate* being weighed. The filtrate is precipitated with sulphuric acid, and the *succinic acid* present deduced from the weight of the precipitate

(233 parts of $BaSO_4 = 118$ parts of $C_4H_6O_4$). The sulphuric acid, succinic acid, and ·0286 allowance for solubility in the tartaric acid estimation are respectively calculated to their corresponding weights of calcium salts, and the sum subtracted from the weight of the mixed calcium salts previously obtained. The difference is the calcium malate, of which 172 parts represent 134 of *malic acid.* The authors of the foregoing process admit that it is tedious, but consider that its accuracy renders it very valuable in important cases. Red wine must be decolorised by animal charcoal before commencing the process.

Further information respecting the determination of succinic, malic, and other fixed acids in wine will be found in the respective articles devoted to those substances. A process for the estimation of succinic acid is also given in the footnote on page 75.

Salicylic acid may be detected by evaporating off the alcohol, agitating the residual liquid with ether, separating the ethereal solution, evaporating it to dryness, taking up the residue with water, and testing the solution with ferric chloride. A fine violet coloration will be produced if the wine contained salicylic acid.

190. In wine which has been "plastered"[1] much of the acid potassium tartrate is converted into free tartaric acid, the proportion of potassium sulphate being correspondingly increased. In unplastered wine, the *sulphates*, calculated as K_2SO_4, do not exceed 0·58 gramme per litre. By the French law, the proportion of sulphates, calculated as potassium sulphate, is limited to 2 grammes per litre, a regulation which is intended to prevent an excessive use of plaster. A good approximate method of estimating the proportion of gypsum in wines is that of Houdart, conducted as follows:—5 c.c. of the wine is measured into each of a series of numbered test-tubes, and to each quantity is added gradually increasing measures of standard barium chloride solution, capable of precipitating the sulphates in 5 c.c. of wine containing, respectively, 1, 2, 3, 4, and 5 grammes of potassium sulphate per litre. Each test sample is raised to the boiling point, and the barium sulphate allowed to settle. A further addition of barium chloride is then made to each test-tube, when the appearance of a turbidity will indicate the presence of unprecipitated sulphate. Supposing the result to have shown a proportion of potassium sulphate greater than 2 but less than 3 grammes per litre, then a fresh series of

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[1] Gypsum, or a gypseous earth, is added to must to give the wine a fiery-red appearance. The gypsum performs a valuable function, as the precipitate formed carries down the albuminous matters and suspended impurities, and gives the wine a clearness which it never has without the use of gypsum. Tartaric acid is sometimes substituted for gypsum.

tests should be made, in which the wine is treated with quantities of the barium solution capable of precipitating 2¼, 2½, and 2¾ grammes of K_2SO_4 per litre. In this manner, the determination may be made to ¼ gramme per litre,—an approximation sufficient for commercial purposes.

191. Sulphates may also be present in wine through the addition of starch-sugar or alum, the latter of which is said to heighten the colour of red wines. They may also be due to the oxidation of sulphurous acid, or even to the direct addition of sulphuric acid (?). In white wines the sulphates may be estimated directly by precipitating 100 c.c. with barium chloride, after adding hydrochloric acid. Of highly coloured wines, 100 c.c. should be precipitated with a slight excess of lime water, diluted to 200 c.c., passed through a dry filter, and the sulphates precipitated in 100 c.c. of the filtrate, after acidulation with hydrochloric acid.

192. Wine casks when musty are often purified by burning sulphur in them, and even bottles are similarly treated to produce earlier ripeness in the wine with which they are subsequently filled. The practice often causes the wine to contain sulphurous acid, which not unfrequently becomes oxidised to sulphuric acid. *Sulphurous acid* can be detected in wine by distilling off the first tenth from 200 c.c. of the sample, diluting the distillate with an equal measure of water, and adding barium chloride and bromine water. A turbidity due to barium sulphate indicates the presence of sulphurous acid in the wine, but the absence of sulphuretted hydrogen should first be proved by testing a portion of the distillate with lead acetate.

193. The *astringent matters* of wine may be determined as described under "Tannins." Nessler and Barth have proposed the following approximate method:—To 12 c.c. of wine add 30 c.c. of alcohol, and filter from the precipitated pectinous and albuminous matters. 35 c.c. of the filtrate, corresponding to 10 c.c. of the original wine, is evaporated to 6 or 7 c.c., and transferred to a somewhat conical graduated tube. Sodium acetate and ferric chloride are then added, and the resultant precipitate measured, after standing 24 hours. 1 c.c. corresponds to 0·033 per cent. of *tannin* in the wine.

194. The *compound ethers* of wine communicate the "bouquet." The volatile ethers are chiefly *ethyl acetate* and *pelargonate*, and the non-volatile *ethyl tartrate*. The total amount of ethers is extremely small, being 0·3 per cent. at the maximum. The proportion of ethers is dependent on the balance of affinities between the acids, alcohol, and water of the wine, and this state of equilibrium always exists in wine of a certain age. The compound ethers of wine may be determined as in par. 294.

DETECTION OF FOREIGN COLOURING MATTERS IN WINE.

195. The artificial colouring of wine is said to be practised with the object of heightening the tint of a red wine deficient in colour, making red wine white, or for colouring wholly factitious wines. Rosaniline, alder-berry, and logwood are among the colouring agents stated to be most frequently employed. A great variety of methods have been devised for the detection of foreign colouring matters, but the majority are not of much practical value.

196. The following method of operating, due to A. Dupré (*Jour. Chem. Soc.*, xxxvii. 572), affords sufficient information for most purposes. The best colourless commercial gelatin (Nelson's) is dissolved in ten parts of boiling water, and the solution poured into a soup-plate or other flat vessel. When cold and thoroughly set a cube about three-fourths of an inch in the side is cut from the jelly by means of a sharp knife and placed in the sample of wine to be tested. After standing twenty-four hours, the cube is removed, washed a little with cold water, and a central slice cut out of it in a direction parallel to one of the sides. On examining this section, it will be found, in the case of a pure wine, that the colouring matter has penetrated but a very little way into the jelly (perhaps $\frac{1}{16}$ of an inch), whereas the great majority of foreign colouring matters will have penetrated to the very centre of the cube.

Of a large number of colouring matters only that of *alkanet-root* resembles the "œnolin" of pure wine in the slow rate at which it diffused into the jelly. Hence, if coloration of the interior of the jelly be not observed, alkanet is the only foreign colouring agent likely to be present. It may be distinguished by its absorption-spectrum, which, at a certain concentration of the acidulated solution, shows three distinct absorption-bands between the sodium line and the blue strontium line, and nearly equidistant from these lines and from each other. Ammonia changes the colouring matter of alkanet to a beautiful blue, and reduces the absorption-bands to two, one coincident with the D line and the other less refrangible than that. Both acid and alkaline solutions produce a general absorption of the blue end of the spectrum, and in moderately concentrated solutions only the red is transmitted.

197. The colouring matter of pure red wine produces a general absorption in all parts of the spectrum except the red, but generally no distinct absorption-band. The red colour is changed to greenish brown on addition of ammonia, and the liquid then shows an indistinct absorption-band in the orange-yellow region.

If the coloration of the cube of jelly points to the presence of a foreign colouring matter, the nature of this may frequently be ascertained, if desired. As a rule, the slice of jelly shows the colour proper to the added substance much more clearly than did the wine itself, and a difference between the two colours is a strong indication of the presence of a foreign matter. *Indigo* and *logwood* may thus be readily discovered. The absorption-spectrum of the light transmitted by the slice will serve for the detection of rosaniline, cochineal, beet-root, red-cabbage, litmus, &c., and further information may be gained by placing the slice in dilute ammonia. Thus treated, a slice coloured with *rosaniline* becomes colourless; with *red cabbage,* dark green; with *cochineal,* purple; and with *logwood,* brown. This last reaction is, however, frequently produced in the absence of logwood. When present, the slice will be coloured brown or yellow to a considerable depth before it is treated with ammonia.

Operating in the above manner, Dupré found that an addition of foreign colouring matter equal to 10 per cent. of the total intensity of the colour of the wine could usually be readily detected, and in no case could 20 per cent. be overlooked. In the case of logwood 5 per cent. could be recognised, and as little as 1 per cent. of rosaniline could be found. In making the tests it is desirable to compare the sample with a pure wine of the same kind.

If the foregoing process does not suffice for the positive recognition of the colouring matter, a larger quantity of the wine should be submitted to dialysis in a parchment-paper dialyser. The diffusate may then be examined, either directly or after careful concentration, by the spectroscope or chemically, the interfering colouring matter of the wine having been eliminated.

A systematic scheme has been devised by A. Gautier (*Jour. Chem. Soc.,* xxx. 330, 428; and xxxii. 935) for the recognition of the foreign colouring matters in wine. It may be advantageously applied to the diffusate obtained as above.

198. *Logwood* may be detected by agitating 20 c.c. of the wine with 2 grammes of finely powdered manganese dioxide, and treating the filtered liquid with zinc and hydrochloric acid, which destroys the brown coloration of the oxidised logwood. The colourless and neutralised liquid, if logwood be present, gives a blue-violet coloration with alkalies and their carbonates, a red-violet with lime water, and a violet with ammonium molybdate in a solution slightly acid with nitric acid. The colouring matter of Brazil wood is the only one which can be confounded with that of logwood.

199. *Rosaniline* salts (fuchsine and magenta) may be detected by rendering 50 c.c. of the wine slightly alkaline with ammonia, and boiling the liquid with a little white wool till all the alcohol and ammonia are expelled. The wool is then removed, washed, and at once heated with a few drops of solution of soda till dissolved. After cooling, about 5 c.c. of water and the same measure

of alcohol are added, and the liquid is shaken up with 10 c.c. of ether. On separating the ethereal layer and adding to it a drop of acetic acid, a red or pink colour will be developed if a mere trace of rosaniline be present. For the detection of somewhat larger quantities, it is sufficient to render the wine alkaline with ammonia, agitate with ether, and shake the separated ethereal solution with dilute acetic acid, when a rose coloration will be produced.

Nessler and Barth render this method roughly quantitative by agitating 100 c.c. of the wine with 30 c.c. of ether and 5 c.c. of strong ammonia. 20 c.c. of the ethereal layer are removed with a pipette and evaporated in a capsule containing a thread of white wool 5 centimetres in length. Similar threads are dyed with known quantities of magenta, and from a comparison of tints the amount of the added colouring matter in the wine is inferred. Very minute quantities of rosaniline may thus be determined. The standard threads may be preserved unchanged in sealed tubes kept in the dark.

200. Another method of detecting rosaniline is to precipitate the wine with basic acetate of lead, filter, and agitate the clear liquid with amylic alcohol, which extracts the rosaniline together with any archil or persio. The two latter colouring matters are used for imitating the colour of sparkling white wines. On adding hydrochloric acid to the separated amylic alcohol, any pink colour due to rosaniline is changed to yellow and destroyed by excess of the acid. The colours due to *archil* and *persio* are unaffected by acid, but changed to violet by ammonia, while the pink of rosaniline is decolorised by the latter reagent.

201. The detection of foreign colouring matters in wine is not of sufficient practical interest, in England at least, to require further description in this work. A very complete account of Gautier's and other methods of examination will be found in A. Wynter Blyth's valuable work on *Foods: their Composition and Analysis.*

202. **Artificial Wines** are manufactured extensively, and sold either alone or in admixture with a certain proportion of genuine wine. A careful analysis and comparison of the results with those yielded by genuine wine of the same supposed character will often, though not always, suffice for the detection of the factitious article.[1]

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[1] As examples of the nature of the probable ingredients of spurious wine, the following recipes are instructive:—

Port Wine.—30 gallons of cider, 5 of spirit, 4 of plain syrup, ½ lb. gum kino, ¼ lb. tartaric acid, and 6 to 8 ounces of "port wine flavour." To produce a better quality add a few gallons of German cherry juice, or any kind of pure wine, Spanish being the best.

Bordeaux or Claret.—To a decoction of 1 lb. of orris root in 5 gallons of water, add 1 gallon of raspberry juice, 2 gallons of pure spirit, ½ lb. "essence of claret," 1 gallon of sugar syrup, and the colouring produced from cochineal.

203. Cider and Perry.

Cider and perry are alcoholic liquids obtained by the fermentation of apple and pear juice respectively.

The following analyses by R. Kayser (*Dingl. Polyt. Jour.*, ccxlviii. 347) show the composition of the filtered must from Borsdorf apples, and of the cider produced by its fermentation.

	Grammes per 100 c.c.	
	Must.	Cider.
Total solid matter,	16·25	2·36
„ „ yielding ash,	0·35	0·31
Alcohol,	...	4·6 (= 5·8 c.c.)
Malic acid,	0·330	0·300
Acetic acid,	...	0·080
Sugar,	12·500	0·750
Pectins,	0·620	traces.
Glycerin,	...	0·680
Potash,	0·106	0·105
Lime,	0·025	0·024
Magnesia,	0·018	0·018
Phosphoric acid (P_2O_5),	0·024	0·022
Sulphuric acid (SO_3),	0·009	0·008

The following are results by other observers :—

	Average of 20 samples of Brittany Cider (Rousseau).	Composition of good ordinary Cider, one year old (Rabot).
Alcohol (by volume),	2·05 per cent.	5 to 6 per cent.
Total solid matter,	1·93 „	3 „
„ „ containing, sugar,	·25 „	...
„ „ mineral matter,	·15 „	0·28 „

From these analyses, it appears that the solid matter of cider differs from that of wine in the presence of malic acid, in the absence of tartaric acid, and by the larger proportion of lime which it contains. By a judicious addition of tartaric acid, or of wine containing much acid, a product might be obtained which would be difficult to distinguish from real wine.

204. Perry is richer in alcohol than cider, as might have been expected from the greater proportion of sugar in pears. The proportion of sugar contained in samples of cider made from six

varieties of apple has been determined by M. Truelle. From the fact that a portion of the sugar exerts no reducing action on Fehling's solution, cider appears to contain traces of cane sugar, or possibly some peculiar variety of sugar.

205. Cider is liable to several diseases, including a formation of acetic acid through secondary fermentation. Another curious affection is the "killing" or blackening, due to the conversion of the malates into carbonates under the influence of a ferment. Cider so affected becomes of a violet-black colour, a symptom which may be remedied by addition of tartaric acid.

206. Cider is liable to be sophisticated by addition of *water*, *colouring-matters*, &c.; by the use of lime, chalk, soda, &c., as *anti-acids*; and by the addition of alum, litharge, white-lead, or sugar of lead as *clarifying agents*. Zinc and copper have also been met with.

Heavy metals may be sought for as described in par. 39.

The presence of *free mineral acids* in cider may be detected as described in the section on vinegar.

Alcohol is often added to weak cider to prevent acetous fermentation.

Factitious Cider is sometimes prepared by fermenting starch-sugar, and adding vinegar, cinnamon, and flavouring ethers.

207. Malt Liquors; Beer; Ale.

Beer is popularly supposed to be a fermented liquor brewed from malt, and having a bitter flavour communicated by hops. This description must be extended considerably to embrace modern beer and its allies, which are defined by Blyth as "fermented saccharine infusions to which a wholesome bitter has been added."[1]

Under the present law of England, the malt of typical beer may be replaced by any saccharine or amylaceous substance, and as the duty is levied on the quantity of soluble carbohydrates made into beer, as estimated by the specific gravity of the infusion, the exact nature of the fermentable matter employed is a matter of indifference to the Excise. Similarly, since the removal of the duty, the employment of hops is not insisted on by the Excise, and any wholesome or *quasi*-wholesome bitter (*e.g.*, quassia, gentian, &c.), can be employed. The substitution is not an infringement of the Sale of Food and Drugs Act, which could, however, be enforced in the case of a distinctly unwholesome bitter being used.

208. *Chemically*, beer and other malt liquors are very complex liquids, of which the main constituents may be conveniently arranged in the following three classes:—

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[1] Under the Bavarian law, beer is a fermented liquid prepared only of barley-malt, hops, yeast, and water.

a. The *volatile constituents;* including alcohol, water, acetic acid, carbonic acid, &c.

b. The *fixed organic matters*, forming the organic constituents of the "extract"; including sugars, dextrin and dextrinoid bodies, albuminoids, glycerin, lactic and succinic acids, organic extractive matters from hops and other bitters, &c.

c. *The mineral constituents* or *ash;* consisting chiefly of the phosphates of potassium, calcium, magnesium, &c.

209. Beer differs from wine in its smaller content of alcohol, and the greater proportion of dextrin and other extractive matters present; also in the absence of tartaric acid, which is characteristic of wine, as malic acid is of cider and lactic acid of beer. The acidity of beer is frequently ascribed to acetic acid, but, except in sour ales, it is chiefly due to lactic acid. A ferment producing lactic acid is present to a greater or less extent in most yeast, and a certain proportion of succinic acid is a constant product of the vinous fermentation of sugar.[1]

210. The composition of malt liquors varies widely according to the nature and proportion of the materials used, and the manner in which the fermentation has been conducted. Broadly speaking, two distinct methods of brewing are pursued, namely, the German and the English. German beers are fermented at a low temperature, under which condition the yeast remains at the bottom of the liquid, and the process is said to be one of "bottom-fermentation." The yeast is a different variety from that of English breweries. Beer brewed on this system contains less alcohol, and more dextrin, sugar, and albuminoids than English beer, and hence is liable to undergo secondary fermentation unless kept at a very low temperature, or else sterilised and preserved in bottles. The German beer also contains less hops and more carbonic acid than English beer. In the English system of brewing, the operation is one of "surface-fermentation," and, as a rule, the product is richer in alcohol and contains less extractive matter than German beer. The different varieties of English beers may be classified as follows (C. Graham, *Proc. Soc. Chem. Ind.*):—

Bitter ales have a high attenuation, high percentage of alcohol, and much hop-extract; *mild ales*, less attenuation, less alcohol, and less extract; *porter*, attenuation much the same as mild ales, but less hops; *stout*, still less attenuation, and less alcohol, and, like porter, but little hop is used, the caramelised products of the burnt malt serving for its preservation.

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[1] The relationship existing between glucose, lactic acid, and acetic acid is well shown by a comparison of their formulæ, *one* molecule of glucose, $C_6H_{12}O_6$, having the composition of *two* molecules of lactic acid, $C_3H_6O_3$, or *three* of acetic acid, $C_2H_4O_2$.

Composition of various Typical Beers (Graham).

		Burton Ales.			Mild X.	XXX.	AK Bitter.	Somersetshire Ale, 2 Years Old.	Scotch Export Bitter.	Dublin Stout XX.	Dublin Stout XXX.	German Beers.					
		Mild.	Pale.	Bitter.								Vienna Lager.	Pilsen Lager.	Munich Lager.	Tivoli (sold in London).	Bohemian (Average).	Bavarian (Average).
Non-Volatile.	Maltose,	2·13	1·75	1·62	1·87	2·88	0·81	1·54	1·62	3·45	5·35	1·64	0·69	1·57	1·75	0·57	0·87
	Dextrin,	3·64	2·48	2·60	1·88	2·04	0·75	2·48	2·50	3·07	2·09	2·74	2·65	3·15	2·15	2·14	3·26
	Albuminoids (Wanklynised),	0·26	0·21	0·16	0·20	0·20	0·21	0·42	0·30	0·26	0·43	0·36	0·20	0·40	0·17	...	...
	Lactic and Succinic Acids,	0·18	0·14	0·17	0·14	0·10	0·14	0·64	0·09	0·17	0·25	0·13	0·09	0·14	0·12	...	...
	Ash, Colouring Matters, and Hop Extract (by difference),	0·53	0·55	0·87	1·30	1·48	0·85	0·94	0·70	1·76	1·40	1·12	0·59	1·82	1·39	...	...
	Total Solid Matters,	6·74	5·13	5·42	5·39	6·80	2·76	6·02	5·21	8·71	9·52	5·99	4·22	7·08	5·58	3·97	6·17
Volatile.	Acetic Acid,	0·01	0·02	0·01	0·04	0·02	0·06	0·07	0·16	0·01	0·04	0·02	0·02	0·01	0·02	...	...
	Alcohol,	6·78	5·37	5·44	4·60	6·50	4·69	6·50	5·00	5·50	6·78	4·69	3·29	4·75	5·31	3·81	4·14
	Water (not determined),	...	...	..	...	...	...	...	...	...	...	...	...	...	...	...	...
	Total Nitrogen (by Soda Lime).	...	...	...	...	...	...	...	...	...	...	0·134	0·090	0·400	0·060	...	...
	Specific Gravity of Beer,	...	...	...	...	...	...	...	...	...	...	1016·5	1011·8	1021·0	1014·0	1008·0	1016·0
	Original Gravity of Wort,	1080·0	1062·0	1064·0	1055·5	1078·7	1044·6	1071·0	1057·0	1074·0	1089·0	1058·6	1040·8	1064·0	1062·0	1048·5	1055·0
	Ratio of Maltose to Dextrin,	1:1·7	1:1·4	1:1·6	1:1	1:0·7	1:1	1:1·6	1:1·5	1:0·88	1:0·39	1:1·66	1:3·8	1:2	1:1·23	1:3·75	1:3·75
	Ratio of Solids to Alcohol,	1:1	1:1·05	1:1	1:0·85	1:0·96	1:1·7	1:1·08	1:0·96	1:0·63	1:0·71	1:0·78	1:0·8	1:0·67	1:0·95	1:0·96	1:0·67

211. The foregoing analyses of typical malt liquors are selected from among those published by C. Graham (*Proc. Soc. Chem. Ind.*). The figures are grammes per 100 c.c. of the sample.

212. These analyses show, in a striking manner, the influence of the mode of brewing on the character of the beer produced. Not only does the proportion of alcohol vary in beers brewed from worts of approximately the same densities, but, owing to the different systems of mashing and fermenting, the German beers are much richer in dextrin than the English. Thus, in the "Mild X" the proportion of maltose to dextrin is 1 : 1; while in the average of Bavarian beers (of nearly the same original gravity) it is 1 : 3·75. The dextrin in beer causes the sense of fulness in the palate, the albuminoids and carbonic acid tending to increase this effect.

213. The following table illustrates in a general manner the composition of various typical varieties of malt liquor. The analyses might be multiplied indefinitely, without adding materially to the information conveyed by the table.

Description.	Specific Gravity.	Alcohol.	Solid Matter or Extract.	Ash.	Free Acid as $C_2H_4O_2$.	Authority.
Pilsen Lager, . .	1013·0	3·55	5·15	0·20	...	Kohlrausch.
Hanoverian (average of 20 samples), . .	1017·0	4·01	6·34	0·24	...	Scalweit.
American Lager (average of 19 samples), .	1016·2	2·78	6·05	0·30	0·12	Engelhardt.
Manchester public house Beer (average of 8 samples), ...	1007·2	4·58	3·64	0·33	0·16	Estcourt.
Salford public house Beer (average of 61 samples),	1011·3	5·00	4·89	0·30	0·24	Carter Bell.
Bass' Pale Ale, . .	1013·8	6·25	6·98	...	0·14	Laurence and Reilly.
Allsopp's Pale Ale, .	1014·4	6·37	4·44	...	0·24	,,
Guinness' xx Stout, .	...	6·66	7·24	...	0·20	,,
Guinness' x Stout, .	1124·4	5·05	5·48	...	0·23	,,
Barclay & Perkin 's Porter, ...	...	5·40	6·00	...	...	Kayser.

CHEMICAL ANALYSIS OF MALT LIQUORS.

214. The determination of the *alcohol* in beer may be effected as described in par. 173.

215. The proportion of *extract* or *non-volatile matter* in beer may be deduced, with a considerable approach to accuracy, from the density of the de-alcoholised liquid, obtained by evaporating the sample to one-third, and diluting it again to exactly its original bulk. The specific gravity of the "extract" is then carefully observed, and the excess above 1000 divided by 3·86, when the dividend is the number of grammes of dry extract contained in 100 c.c. of the beer. C. Graham considers the estimation of the

solid matter of beer from the density to be untrustworthy, and always determines the extract by evaporating the liquid so as to form a *thin* film, which is dried for many hours till the weight is constant (compare paragraph 180). The determinations of extract in the beers, the composition of which is given in the table on page 92, were made in this manner.

216. The *ash* of beer is determined by igniting the extract, with due precautions (par. 95 *et seq.*). The proportion of ash should bear a due relation to the original gravity of the wort, an excess indicating the addition of some mineral substance. Calcium sulphate may be present, owing to the beer being partially brewed from starch-sugar, or from the oxidation of calcium sulphite, now largely employed as a preservative. Excess of calcium or magnesium, without a corresponding excess of sulphates, may be due to the use of an earthy carbonate as an anti-acid. The proportion of phosphoric acid in beer is occasionally of interest, and is determined most accurately in the ash of the beer (see par. 101), but, in the case of light-coloured beers, very fair comparative results may be obtained by a direct titration of the liquid with a standard solution of uranium. Common salt is added to beer less frequently than formerly, and is rarely employed in excessive quantity.[1] A rough idea of the amount may be obtained by estimating the *chlorides* (with the precautions mentioned in pars. 95 and 101), but for the accurate determination of the salt the actual isolation of the sodium chloride in a pure state is essential. This involves the evaporation of the previously neutralised beer, cautious ignition of the residue, isolation of the mixed chlorides of the alkali metals by the processes of mineral analysis, precipitation of the potassium as chloroplatinate, and recovery of the sodium chloride from the filtrate.

217. The *sugar* and *dextrin* of beer may be determined as described under "Malt."

218. The total nitrogen of beer may be determined by igniting the dry extract with soda-lime. The proportion obtained is usually multiplied by 6·33 and the product stated as the *albuminoids* of the beer, but this method is misleading, as there are other nitrogenous matters present besides albuminoids. On this account, C. Graham prefers, for practical purposes, to estimate the "*albumi-*

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[1] It is sometimes stated that the addition of salt to beer, in a proportion not exceeding 50 grains per gallon, is directly permitted by the law. This is an error, the origin of which was that the Board of Inland Revenue instructed their officers that, in cases in which the chlorides in beer did not exceed the equivalent of 50 grains of common salt per gallon, it was unnecessary to inquire into the origin of the chlorides.

noid ammonia" in 1 c.c. of the beer, by diluting it largely with water, and distilling it first with sodium carbonate and then with alkaline permanganate, as in Wanklyn's method of water analysis. The albuminoid ammonia found is multiplied by the factor 5·2, the product being the equivalent of albuminous matters or proteïds in the measure of beer taken. Graham states that a beer brewed from malt and intended for exportation or storage should not show more albuminoids when "Wanklynised" than 0·01 per cent. for each Bates' degree of original gravity. Thus, a beer having an original gravity of 20 lbs. per barrel (= 1055·5 specific gravity) should not show more than 0·20 per cent. of proteids, by the permanganate process.

219. The *free acids* of beer are partly fixed and partly volatile. The former consist of *lactic* and *succinic* acids, which may be determined jointly in terms of lactic acid by dissolving the dry extract of the beer in water and titrating the solution with standard alkali and litmus paper. 1 c.c. of decinormal soda solution represents 0·009 gramme of lactic acid. The volatile acid of beer is chiefly *acetic acid*, which is usually determined by subtracting the measure of alkali required to neutralise the extract from that required by the original beer (after thorough agitation to get rid of as much carbonic acid as possible). The difference is calculated to acetic acid, 0·006 gramme of which corresponds to 1 c.c. of decinormal alkali.

The real *succinic acid* and the *glycerin* may be determined as described in the footnote on page 75. Calcium *lactate* may be separated from the impure succinate by boiling with spirit of 80 per cent., which dissolves the lactate only.

220. *Salicylic acid* is now frequently added to beer as a preservative. It may be searched for by concentrating the beer to one-half at a gentle heat, and shaking the cold liquid with ether. The ethereal layer is separated, evaporated to dryness, and the residue dissolved in warm water. On adding ferric chloride, a violet coloration will be produced if salicylic acid be present.

221. Occasionally it is of interest to determine the *carbonic acid* of beer. This may be effected by adding a little tannin to 100 c.c. of the sample, and boiling the liquid in a capacious flask attached by a bent tube to absorption-bulbs containing baryta-water. When the gas is wholly driven off from the beer, the baryta-water is filtered (avoiding contact with the air), and the carbonic acid deduced from the weight or neutralising power of the precipitated barium carbonate.

222. *Glycerin* and *hop-resin* may be determined, according to Griessmayer (*Deut. Chem. Ges. Ber.*, xi. 292), by slowly evaporat-

ing 300 c.c. of the beer to a volume of 100 c.c., and shaking the concentrated liquid with 200 c.c. of petroleum ether. When separation has taken place, the upper layer is removed, and the lower layer again shaken with petroleum ether. The petroleum extract is evaporated on a water-bath, and the residual hop-resin dried over sulphuric acid and weighed. The aqueous liquid separated from the petroleum ether is rendered alkaline with baryta, and then shaken with twice its measure of a mixture of two volumes of alcohol with three of ether. The upper layer is separated, and the denser liquid again agitated with ether-alcohol. The ether-alcohol extract is heated on a water-bath till the ether is driven off and the residual alcoholic liquid evaporated in successive small portions in a porcelain dish till it acquires a syrupy consistence, when it is further dried for two days over sulphuric acid and the residual glycerin weighed.

DETECTION OF BITTER SUBSTANCES IN BEER.

223. Very elaborate processes has been devised by Dragendorff, Wittstein, and others, for detecting the presence of substances which might possibly be used for imparting a bitter taste to beer, but these methods have little practical interest in the present state of the English law, and hence it will be sufficient to describe the method of searching for the more commonly used "hop-surrogates," and certain objectionable substances the occasional employment of which is suspected.

224. For the detection of noxious bitters, A. Dupré recommends the following process:—Evaporate 1 quart of the beer to a thin syrup, and add very gradually 1 pint of pure rectified spirit, stirring all the time. Allow the syrup to stand for fifteen minutes, pour off the spirit from the heavy residue, and distil it to a small bulk. Treat the residue in the retort with water and sufficient soda solution to render it alkaline, and agitate it several times with ether. Separate the ethereal stratum, which contains the bitter principle of the hop, any alkaloids which may be present, resinous matter, and fat. The alkaline liquid is next acidulated with acetic acid, and again agitated with ether. The ethereal layer is separated, evaporated, and the residue taken up with water and added to a pint of water in which some minnows or other small fish are placed. If they fall over on their sides, or die outright, some noxious material has been added to the beer. This poisonous action on fish is often described as specially characteristic of *picrotoxin*, the active principle of *Cocculus indicus* or Indian berry.

225. The systematic method of examining beer for bitter substances detailed in the following table, is based chiefly on the recommendations of Enders:—

<table>
<tr><td colspan="7">Evaporate 1 litre of beer to a syrup over the water-bath, mix the residual liquid with five measures of strong alcohol, allow the solution to stand for twenty-four hours, filter from the dextrinous precipitate, and add ether to the filtrate as long as a further precipitate is produced. The filtered liquid is evaporated to a low bulk, the residue treated with alcohol, and the solution diluted with water, precipitated with lead acetate, and the precipitate filtered off.</td></tr>
<tr><td colspan="2" rowspan="2">The Precipitate is washed, suspended in water, decomposed by sulphuretted hydrogen, the sulphide of lead filtered off, washed with alcohol, and the filtrate and washings evaporated to dryness at 100° C. The residue is dissolved in chloroform, the solution warmed with water till the chloroform is driven off, and the liquid filtered.</td><td colspan="5">The Solution is freed from lead by sulphuretted hydrogen, filtered, and evaporated to one-half. It will be free from bitter taste if no hop substitutes were used, as the hop-bitter is entirely precipitated by lead acetate. If bitter, the solution is precipitated with tannin and filtered.</td></tr>
<tr><td colspan="4">The Precipitate is mixed while moist with lead carbonate, dried, boiled with alcohol, and the solution filtered, evaporated to a small bulk, and shaken with ether.</td><td rowspan="4">The Solution may contain picrotoxin. It is acidulated with sulphuric acid and shaken with benzene to remove picric acid and other bitter principles, and then agitated with chloroform. The chloroform layer is separated and allowed to evaporate spontaneously, when any <i>picrotoxin</i> (from <i>Cocculus indicus</i>) will remain as a bitter substance, which is deposited from its solution in hot alcohol in feathery crystals, having a characteristic appearance under the microscope. If the chloroform residue be dissolved in water and added to about 100 c.c. of water containing a minnow or stickleback, the fish will speedily fall over on its side if picrotoxin be present. This test is not peculiar to picrotoxin.</td></tr>
<tr><td rowspan="3">The Residue, if bitter, consists of <i>hop-bitter</i>.</td><td rowspan="3">The Solution, on evaporation to dryness, leaves <i>lupulin</i> (from hops), which is bitter; has an acid reaction; is soluble in water, alcohol, and chloroform; does not reduce ammonio-nitrate of silver; and is not precipitated by tannin from its solution in proof spirit.</td><td rowspan="3">The Ethereal Layer on evaporation leaves <i>absinthiin</i> (from wormwood), soluble in strong sulphuric acid with brownish colour, changing to violet-blue on cautious dilution with water. Absinthiin has a peculiar odour and intensely bitter taste: reduces ammonio-nitrate of silver on heating, but not Fehling's solution; and is precipitated by tannin, but not by lead acetate.</td><td colspan="3">The Aqueous Liquid is agitated with chloroform, the aqueous layer separated, and the chloroform evaporated to dryness. A portion of the residue, if bitter, is dissolved in warm water and solution heated with ammonio-nitrate of silver.</td></tr>
<tr><td colspan="2">Reduction of metallic silver may be due to gentipicrin or menyanthin. Test a portion of the chloroform residue with strong sulphuric acid.</td><td rowspan="2">No Reduction. The chloroform residue, if intensely bitter and coloured brown by ferric chloride, probably contains <i>quassiin</i>, which gives little or no colour with sulphuric acid, but is precipitated by tannin.</td></tr>
<tr><td>Red colour on warming indicates <i>gentian bitter</i>, the aqueous solution of which gives a brown-green colour with ferric chloride.</td><td>Yellowish brown colour, changing to violet-red, indicates <i>menyanthin</i> (from <i>Menyanthes trifoliata</i>, or buck-bean), which on heating with dilute sulphuric acid gives menyanthol, having an odour like oil of bitter almonds.</td></tr>
</table>

378

Of the bitter principles the detection of which is described in the foregoing table, picrotoxin is the most objectionable.

226. For the detection of *picric acid* a variety of methods have been proposed, but the best, in the opinion of the author, is as follows:—Evaporate 100 c.c. of the beer to about one-third, acidulate with sulphuric acid, and agitate with ether or petroleum ether. The ethereal layer is separated, evaporated at a gentle heat, and the residue dissolved in hot water. The solution is heated with a fragment of white wool, which in presence of the smallest trace of picric acid will acquire a yellow colour. Amylic alcohol has been proposed as a substitute for ether, but is not so satisfactory. The reaction may be confirmed by treating the wool with very dilute ammonia, filtering, and evaporating the filtrate on the water-bath to very small bulk. On adding a few drops of cyanide of potassium solution, and heating, a distinct red colour will be produced in presence of picric acid.

227. DETERMINATION OF THE ORIGINAL GRAVITY OF BEER WORTS. As the duty on beer (as was formerly that on malt) is calculated from the strength of the wort as indicated by its specific gravity, it becomes necessary to allow a rebate or drawback when the beer is exported. If the wort could always be examined in an unfermented state, it would merely be necessary to ascertain its density and gauge its measure to obtain the data for calculating the allowance to be made. But, by the process of fermentation, the specific gravity of the wort is diminished to an extent dependent on the amount of alcohol formed. The weight of alcohol produced being approximately 50 per cent. of the saccharine matter destroyed by the fermentation, it is evident that a determination of the alcohol in the fermented liquid would give the means of ascertaining the quantity of sugar destroyed, and hence of making the necessary correction for the reduction in the density of the wort (technically called its "attenuation") caused by the fermentation.

The practical details of the methods of determining the original gravities of beer worts have been very carefully investigated by Messrs Graham, Hofmann, and Redwood,[1] and their results show that the desired information can be obtained with great accuracy in the following manner:—

228. *a. Distillation Method.*—A known measure of the beer (4 fluid ounces, or 100 c.c.) is distilled, without addition of soda or tannin, in an apparatus furnished with a good condensing arrangement, as described in par. 163 *b*. When about half the liquid has passed over, the distillate is diluted with water till it occupies,

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[1] *Report on Original Gravities*, 1852.

at 60° F., the exact original bulk of beer taken, when its specific gravity is carefully observed. The difference between 1000 and the gravity of the distillate is called the "spirit indication" of the beer. Reference is next made to the following table, from which is ascertained the number of "degrees of gravity lost" by the attenuation of the wort.

The figures in the table are identical with those in Schedule I. of the Inland Revenue Act, 1880, and were deduced from actual experiments on malt worts fermented under normal conditions, in the manner detailed in Graham, Hofmann, and Redwood's Report.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	...	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·4	75·3	75·9

229. These conditions included the formation of one part of acetic acid ($C_2H_4O_2$)[1] in 1000 measures of the beer, and hence no correction is necessary in the case of beers containing about this proportion, but the free acid in old and hard beer is often very sensibly in excess of the above named amount, and in such cases its percentage must be determined by titrating the beer with standard alkali.[2] Any excess of acetic acid thus found, above

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[1] As already stated the normal acidity of beer is really due more to lactic and succinic acids than to acetic acid.

[2] This may be effected as described in par. 185 ; or the standard solution of caustic soda may be replaced by standard ammonia. This is made by diluting ordinary solution of ammonia with distilled water till it has a density of ·9986 at 60° F. 100 c.c. of such a solution will exactly neutralise 1 gramme of acetic acid ($C_2H_4O_2$) or 1·050 grammes of crystallised oxalic acid, and hence 100 fluid grains are equivalent to 1 grain. If 100 c.c. of beer be employed for the titration each 1 c.c. of ammonia employed represents 0·01 per cent. of free acid.

2834:

the 0·1 per cent. normally present, must be calculated into alcohol and duly allowed for. This is most readily done by the following equation, in which a represents the percentage of acetic acid (or more strictly speaking, the grammes of free acid reckoned as acetic per 100 c.c. of the beer):—

$$1{\cdot}3a - {\cdot}14 = \text{spirit-indication.}$$

The value $1{\cdot}3a$ gives the spirit indication corresponding to the whole free acid present, and hence from that has to be subtracted ·14, the spirit indication of the natural ·1 per cent. of free acid. Thus, if a beer be found to contain ·48 of free acid calculated as acetic, then the correction of the spirit indication will be—

$$1{\cdot}3({\cdot}48) - {\cdot}14 = {\cdot}484.$$

Hence the figure ·484 (or practically ·48) will require to be added to the "spirit indication" ascertained from the gravity of the distillate of the beer. Except in the case of decidedly sour beers, such as would be very unlikely to be exported, the correction for excess of acetic acid is generally so trifling that it may be neglected.[1]

It remains to dilute the "extract," or liquid left in the retort, with water, till it measures exactly the original bulk of the beer taken, when its specific gravity is to be carefully taken. This is called the "extract gravity."

230. The original gravity of the wort is then ascertained by adding the degrees of "gravity lost" to the density of the extract. The mode of calculation will be seen from the following example:—

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[1] The directions in the Inland Revenue Act of 1880 for ascertaining the original gravity of worts in which fermentation has commenced are as follows. It will be observed that the question of acidity is wholly ignored, as the process is intended to be employed for the examination of recently fermented worts:—

"1. A sample is to be taken from any part of such worts, and a definite quantity thereof by measure at the temperature of 60° Fahrenheit shall be distilled.

"2. The distillate and residue shall each be made up with distilled water to the original measure of the quantity before distillation, and the gravity of each shall be ascertained.

"3. The number of degrees by which the gravity of the distillate is less than the gravity of distilled water shall be deemed the spirit indication of the distillate.

"4. The degrees of original gravity standing opposite to such spirit indication in the table in the first schedule to this Act added to the specific gravity of the residue shall be deemed the original gravity of the worts."

Specific gravity of *water* at 60° F.,	1000·0
Specific gravity of *distillate* at 60° F.,	989·0
Difference = "*spirit indication*,"	11·0
Allowance for alcohol corresponding to ·20 per cent. *excess* of acid,	·26
Corrected spirit indication,	11·26
Equal, by table, to "*gravity lost*,"	50·4
To which add specific gravity of *extract*,	1041·3
Original gravity of wort,	1091·7

231. The table already given (page 99) is the only one legalised for the determination of original gravities, and is used by the Excise, without correction, whether the wort be derived wholly or partly from starch- or cane-sugar, or simply from malt. This practice gives the brewer the advantage of any error. But, for private purposes, it is well to bear in mind that while the table is accurate when applied to beers brewed wholly or partly from starch-sugar instead of malt, it is deficient in accuracy when used for beer brewed from cane sugar, unless a deduction of ·35° be made from the spirit indication before referring to the table. With this correction, necessitated by the increase in density undergone by cane sugar solutions on inversion, the table already given furnishes accurate results.

232. *b. Evaporation Method.*—In employing this process, the specific gravity of the original beer is first carefully ascertained, taking care to agitate the liquid well to eliminate as much carbonic acid as possible. The "extract gravity" is next determined. For this purpose there is no occasion to boil the sample in a closed vessel, as it is not required to collect the volatilised spirit. It is simply necessary to evaporate sufficiently to ensure the entire expulsion of the alcohol, and then allow the liquid to cool, and make it up exactly to the original bulk of the beer taken. The density is then observed, and the corresponding "spirit indication" ascertained by subtracting the density of the original beer from that of the "extract." The necessary allowance, if any, for excess of acid above 0·1 per cent. must next be made as in the distillation method, and from the corrected spirit indication the corresponding number of degrees of gravity lost is ascertained by reference to the table already given. The result thus obtained is not in strict accordance with that by the distillation method, and requires to be corrected by an addition of

$\frac{1}{40}$ to the "degrees of gravity lost" as ascertained by the table. Thus, if the corrected spirit indication be 9·4, corresponding to 41·2 degrees of gravity lost, the last figure requires a correction of $\frac{41\cdot2}{40}=1\cdot03$, which, added to 41·2, raises it to the corrected number, 42·03 degrees. The following example illustrates the whole mode of calculation :—

Specific gravity of "*extract*,"	1044·7
Specific gravity of original *beer*,	1035·2
Difference = "*spirit indication*,"	9·5
Allowance for excess of acidity,	0·1
Corrected spirit indication,	9·6
Corresponding "*gravity lost*" (by table),	42·2
Correction of $\frac{1}{40}$ of above number,	1·055
Corrected gravity lost,	43·25
Specific gravity of *extract*,	1044·7
Original gravity of wort,	1087·95

233. The results by the evaporation process are not generally so reliable or so constant on repetition as those by the distillation method, but they are obtained with great facility, the only additional operation necessary being the determination of the density of the original beer, and hence the calculation should never be omitted, as it furnishes a valuable check on the distillation process. If the wort is a solution of cane sugar, a deduction of ·35 should be made from the spirit indication as described in par 231.

Other methods of determining the original density of beer worts have been devised by Balling and others, but practically the processes already described are amply sufficient for the purpose.

234. **Spirits.**

Under the term of spirits are comprehended the various liquids obtained from alcohol-containing liquors by distillation. Wheat, oats, rye, barley, Indian corn, rice, and other grains, whether in the raw or the malted state, as well as the juices of fruits, sugar-cane, beet-root, potatoes, carrots, and even some of the grasses, may be made to yield alcohol by fermentation. When the resulting alcoholic liquid is distilled, a "spirit" is obtained, which is known under various names, according to circumstances. Thus, British spirit (whether brandy, gin, whisky, or rum) is produced from grain; "cognac," or French brandy, from wine; West Indian rum, from sugar or molasses. The different characters of these various liquids depend partly on the percentage of alcohol contained in them, partly on the mode of manufacture pursued, partly on the berries, seeds, herbs, &c., with which they are flavoured, and, lastly, on the substances from which the spirits are derived.[1] The object of the distillation is, of course, in every case to separate the alcohol from the non-volatile matters, such as husk, fibre, inorganic salts, undecomposed yeast, lactic and succinic acids, glycerin, &c. The volatile products are, besides water, chiefly ethylic alcohol, fusel oil, acetic acid, and traces of ethers. The presence of fusel oil is very objectionable (see par. 260), and one of the chief objects of the distiller should be so to manage the process as to effect its separation from the spirit as completely as possible. This can be partially done by careful distillation alone; but soap, milk, charcoal, and other "physics" are also of more or less service.

The first operation, or "distillation," produces a crude alcohol, which is redistilled or "rectified." The prosecution of this process constitutes a distinct business from that of the distiller proper.

235. ARRACK is a name which is properly applied to a spirit distilled from toddy, the juice of the cocoa-nut tree. Batavian and Jamaica arrack are, however, manufactured from molasses and rice, with a little toddy, and hence are really varieties of rum. Arrack usually contains somewhat more than 50 per cent. of alcohol, and mere traces of extractive matter.

236. BRANDY, strictly speaking, is a spirit obtained by the distillation of wine. The "marc" of grapes and other refuse products obtained in the manufacture of wine are frequently employed for the production of an inferior quality of brandy. Such a product contains much more fusel oil than is present in the superior variety. The peculiar flavour and aroma of "cognac," or French brandy, are due to the presence of ethyl pelargonate ("œnanthic ether"), and other secondary products of fermentation. When freshly distilled, brandy is perfectly colourless, but it readily takes

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[1] The spirit produced by the fermentation of molasses contains a notable quantity of aldehyde, while that from rye contains less of this body but more amyl alcohol. Healthy, well-cultivated yeast produces a pure alcohol, but if sickly and imperfectly developed the proportion of amyl alcohol, &c., is largely increased. A rough method of testing raw spirit consists in treating the sample with an equal measure of strong sulphuric acid, and heating the mixture for fifteen minutes in boiling water. The more impure the spirit the deeper the yellow or brown colour which is produced.

up colouring matter from the storing casks, and *caramel* and similar colouring agents are frequently added to it. It often contains traces of tannin and free acid. Artificial or British brandy is manufactured by flavouring grain spirit. Among the flavouring agents employed for the purpose are acetate, nitrite and pelargonate of ethyl; oils of cassia, cloves, and bitter-almonds: tinctures of allspice, galls, capsicum, oak-bark, &c.; burnt sugar, and other colouring materials. Another very perfect imitation cognac is prepared by distilling proof spirit with argol, bruised prunes, and a little real cognac. The distillate is then coloured with caramel and flavoured with tannin.

237. GIN is a colourless neutral spirit, originally obtained from grain. The grain spirit is treated with oil of juniper, turpentine, or other flavouring agents, and again distilled. Gin is usually very free from fusel oil, free acid, tannin, &c. Sugar is a normal constituent of sweetened gin. Salts of zinc and lead have occasionally been met with in gin, and alkaline solutions, such as carbonate of potassium, are sometimes added. Among the substances used for flavouring gin are juniper berries, oil of juniper, turpentine, almond-cake, coriander seeds, cardamom seeds, grains of paradise, capsicums, calamus, orris and angelica roots, &c. Gin is frequently largely diluted with water.

Hollands and Schnapps are varieties of gin.

238. KIRSCHWASSER, or KIRSCH, is a spirit obtained by the distillation of the fermented juice of the wild cherry. It is prepared chiefly in the Black Forest, Switzerland, and certain departments of France.

Kirschwasser usually has an alcoholic strength of about 10° U.P. It contains, as a normal constituent, a small proportion of prussic acid. In good kirsch this usually amounts to not more than 0·15 gramme per litre, but inferior specimens often contain three or four times this amount. Barth found hydrocyanic acid in all of 29 samples of kirschwasser from cherries, and in two samples made from plums, other samples being free from it. Kirschwasser also frequently contains distinct traces of *copper*; and so constantly is this metal present, that it has been regarded as indicating the genuine nature of the spirit. It is evident that this presumption is very fallacious, as the presence of copper entirely depends on the use of an apparatus of that metal for distillation, and could readily be added to a spurious article. If present, the copper may be detected and estimated by evaporating the spirit to dryness, igniting the residue, dissolving in dilute nitric acid, and estimating the copper colorimetrically. Barth found proportions varying from *nil* to 0·015 gramme of cupric acetate per litre.

Kirschwasser is often mixed with alcohol from other sources, or is made entirely from grain spirit, flavoured with peach blossoms or cherry-laurel leaves. The excessive proportion of hydrocyanic acid in such preparations indicates their origin. The addition of cherry-laurel water is indicated by the same means. According to Boudet, such kirschwasser contains ·220 grammes of HCy per litre. A preparation is sometimes sold as kirschwasser, consisting of dilute alcohol, somewhat sweetened and flavoured with oil of bitter almonds, and occasionally nitro-benzene has been substituted for the last ingredient. These additions may be detected by distilling off the alcohol at a low temperature, shaking the residual liquid with ether, and examining the ethereal solution for benzoic aldehyde and nitro-benzene.

The absence or presence of calcium compounds and other mineral matters have been sometimes regarded as proofs of the genuine or factitious character of kirschwasser, but such impurities occur in undoubtedly genuine samples.

239. Rum.—This spirit was formerly wholly obtained by distillation of the alcoholic liquid obtained by fermenting the juice of the sugar-cane. It is now made largely from molasses and other residual products of the manufacture of sugar from the sugar-cane, beet-root, &c. The characteristic flavour of rum is due to the presence of ethyl butyrate and formate. Factitious rums are manufactured by flavouring grain spirit with butyric and acetic ethers, or even by adding butyric acid, which gradually forms ethyl butyrate by reacting with the alcohol present. Sliced pine-apples and essence of violets have been employed, and tannin matters are also added. Rum is coloured by burnt sugar, or by long keeping in casks. Beckurts states that the extractive matter of rum consists chiefly of saccharine matter, and has no rotatory action on polarised light.

The presence of formates might perhaps serve to distinguish genuine rum from a factitious product. To detect it, the rum should be evaporated nearly to dryness with a slight excess of soda, and the residue treated with phosphoric acid, and distilled. The distillate from genuine rum will strongly reduce silver nitrate, and give the other reactions of formic acid.

Bay Rum is prepared by distilling the fresh leaves and berries of the bayberry tree (*Myrcia acris*) with rum. The product has density of ·921 to ·938. The fragrance and healing properties of bay rum are probably due to the presence of eugenol. Some of the preparations known as "bay rhum" are prepared from tincture of bay leaves and rose water, with additions of bay oil, borax, &c.

240. **Whisky** is a variety of spirit distilled from fermented grain or potatoes. In some cases the barley, or other grain, is first malted, but in others it is used raw. When unmalted grain is used the first operation produces a crude alcohol which is redistilled; but, when malted grain has been fermented, small stills called pot-heads are employed; the product has a flavour distinct from that produced from raw corn in large stills, and is simply kept for a time and not redistilled. In the majority of cases a judicious admixture of raw and malted grain is employed. Other things being equal, the spirit from malted grain is the most valuable, and contains least fusel oil. Whisky improves greatly on keeping, owing to the conversion of the fusel oil into other bodies.

Whisky usually contains a trace of volatile acid, the proportion of which rarely or never reaches 0·1 per cent. (in terms of acetic acid). When new it is colourless, or nearly so; but by storing in sherry casks—a favourite mode of imparting flavour to whisky—it acquires colour, and then contains sensible traces of tannin, sugar, &c. The residue left on evaporating whisky to dryness on the water-bath should not exceed 100 grains per gallon, and is usually much less. The smoky flavour of Irish whisky is due to the fact that the malt used has been dried upon kilns in which peat is used for fuel, but is often imitated by adding one or two drops of creasote to the gallon of spirits. Logwood, catechu, tea infusion, burnt sugar, &c., are sometimes added as colouring agents. Wood naphtha has been occasionally used as an adulterant of whisky. It is very doubtful whether fusel oil is ever purposely added to whisky, but it is almost invariably present in greater or less quantity, and is the cause of the objectional symptoms produced by new spirit (see par. 260). Alkaline solutions (*e.g.*, carbonate of sodium), salts of zinc, lead and copper, cayenne pepper, and other objectionable matters, have been occasionally added to whisky.

241. Chemical Examination of Spirits.

The chemical analysis of spirits is sometimes very difficult, and in the present state of our knowledge the recognition of the flavouring agents is often impossible. The following are the chief points to which attention should be directed:—

242. *Alcoholic Strength of Spirits.*—The determination of the proportion of alcohol in spirit may be effected with ease and accuracy by the methods detailed in par. 153 *et seq.* By the "Sale of Food Amendment Act" of 1879, the minimum limit of strength for gin was fixed at 35° under proof (= 65 per cent. of proof spirit), and that of brandy, rum, and whisky at 25° under proof (= 75 per cent. of proof spirit). These limits were fixed on the recommendation

of Dr James Bell of the Inland Revenue Laboratory, and certainly do not err on the side of too great stringency.[1] The gin sent out to retailers by the trade is chiefly of two strengths, 17° and 22° U.P., but Messrs Gilbey and a few other firms also supply a still weaker gin at a correspondingly low price. In calculating the proportion of water added to gin, by a retailer, it is well to assume that the spirit sold to him had a strength of 20° U.P. The method of calculation is described in par. 159.

All spirits consist of more or less diluted alcohol, containing small proportions of flavouring agents. When spirits are stored in casks they lose strength with a rapidity depending on their percentage of alcohol, the mode of storage, &c. In an atmosphere saturated with aqueous vapour, the alcohol alone evaporates very rapidly, but in a dry atmosphere water also will volatilise, and hence the spirit will not lose so greatly in strength. By keeping, the fusel oil becomes more or less changed and converted into certain ethers, the presence of which materially enhances the value of the spirit. Hence the alcoholic strength of spirits is not the only factor to be considered in judging of their money value or wholesomeness, although the other considerations are far less tangible.

The detection of *wood spirit* and *fusel oil* may be effected as described in pars. 133 and 271.

243. *The non-volatile residue* is sometimes of importance. When freshly distilled, spirits contain no trace of non-volatile matter. When kept in casks they take up more or less fixed matter, but the amount rarely exceeds 100 grains per gallon. It consists of tannin, colouring matter, sulphates, traces of sugar, &c. The proportion of non-volatile matter in spirits is ascertained by evaporating 50 or 100 c.c. to dryness on a water-bath. Some indication of its nature may be obtained by tasting the residue. On ignition in the air, any zinc, lead, or copper present in the spirit will be left as an oxide. Very sensible traces of these metals may be present accidentally, and there is good evidence that their salts were formerly occasionally used as adulterants. Occasionally, clarifying materials have been employed of which lead acetate formed a constituent. Alum was also used occasionally. The reaction of the ignited residue should be observed, as, if alkaline, an alkaline carbonate, acetate, tartrate, &c., must have been present.

244. *Sulphates* will be detected on adding barium chloride to

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[1] A report by Dr Engelhardt on the quality and strength of the spirits sold in the State of New York, shows that the strength of brandy varied from 46° to 12° U.P.; the whisky from 50° U.P. to 5° O.P.; and the rum from 54° U.P. to 1° O.P.

the diluted spirit. Free sulphuric acid has been met with in whisky, and is said to have been formerly freely used for adulterating gin. This is extremely improbable.[1] The presence of free sulphuric acid may be detected by the methods used for examining vinegar for mineral acids.

245. *Free acid* may exist in brandy, &c., as a natural constituent of the distilled liquid. The amount due to this cause is very small, and the acid so present is wholly volatile. The proportion of total free acid may be ascertained by titrating the spirit with standard alkali, and, if the volatile acid be distilled off from another portion of the sample, the relative proportions of fixed and volatile acid may be ascertained, and calculated to tartaric and acetic acids respectively.

246. *Tannin* is often present in brandy, &c., being chiefly extracted from the casks used for storing. Sometimes it is purposely added in the form of tincture of galls or oak-bark. It may be detected by the darkening produced on adding ferric chloride to the spirit, and any reaction thus obtained may be confirmed by boiling off the alcohol from another portion of the spirit and adding solution of gelatin to the residual liquid, when a precipitate will be produced if tannin be present.

247. *Caramel* (burnt sugar) is used for colouring and flavouring spirits, and is left as a brown residue on evaporating the spirit on the water-bath. It is distinguished by its bitter taste, its power of reducing Fehling's solution, &c. On adding basic acetate of lead and filtering, spirits containing caramel are said to give a yellow or brown solution, but otherwise are decolorised. According to E. Carles, if albumin be added to the diluted liquid and the mixture well agitated and allowed to settle, genuine spirit will be decolorised, but the colour due to caramel is not affected.

248. *Sugar*, when present, must always have been added subsequently to the distillation. Its presence is legitimate in the case of gin, which is more strictly a liqueur than a simple spirit. Gin being perfectly neutral in reaction, the cane-sugar added undergoes no change; but in acid spirits it is usually changed to invert sugar.

249. *Heavy metals*, such as lead and copper, may be detected in the original spirit by sulphuretted hydrogen, with the addition, when zinc is to be sought for, of ammonium acetate. They may also be detected and estimated in the matter left on evaporating the sample to dryness and igniting the residue (see par. 104).

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[1] The author has examined many hundreds of samples of commercial spirits, and has not in any case met with more than slight traces of sulphates. The experience of F. E. Engelhardt in the State of New York is exactly similar.

250. *The flavouring agents* added to spirits are usually employed in such a small quantity that any attempt to identify them is almost hopeless, except under very favourable circumstances. A useful means of concentrating the flavouring matters and ethers consists in adding dry calcium chloride to the spirit, when the alcohol and water are in great measure absorbed, and the other matters become concentrated in the residual liquid. The aroma of spirits and similar liquids is best observed by pouring the liquid into a clean flask, pouring it out again, and noting the odour of the residual vapour.

If the bodies producing the aroma are less volatile than alcohol, they may be conveniently recognised by leaving a long strip of filter paper partially immersed in the liquid, when the essences will become concentrated in the part of the paper exposed to the air. The varied nature of the flavours used is indicated in the description of the special characters of the different kinds of spirits. The various *ethers* employed are, as a rule, more volatile than the remainder of the spirit, and hence become concentrated in the first portions which distil over. In these, they may sometimes be recognised by their odours, and occasionally, but rarely, by their chemical characters.[1] The active principles of a few flavouring agents are fixed, and thus remain in the residue when the spirit is evaporated. This is the case with *capsicum* (cayenne). In spirits flavoured with this material the residue left on evaporation has a hot pungent taste. A still more characteristic property is observed on heating the residue. If capsicum be present, on smelling the fumes an intolerably pungent odour will be noticed, and a burning sensation produced in the lungs. The same effects are obtainable by smelling the fumes arising from heated cayenne pepper. The author has observed the production of the irritant fumes in cases in which the residue was free from marked pungent taste, but he was unable to identify the substance present. Convictions have occurred for selling whisky adulterated with cayenne, but in the great majority of cases cayenne appears to be used as a flavouring agent and not with any idea of imparting a factitious strength to the spirits. *Nitro-benzene* has been added to spirits; but the quantity used must be very small. It may be detected by distilling off the alcohol, agitating the residue with ether, removing the ethereal layer with a pipette, allowing the solvent to evaporate, and boiling the residue for some time with zinc and dilute hydrochloric acid, whereby the nitro-benzene is reduced to aniline. The liquid is next diluted, neutralised with caustic soda, and a clear solution of bleaching powder cautiously added. A blue or purple coloration, often appearing somewhat slowly and gradually changing to brown, will be produced if aniline be present, thus indicating the previous existence of nitro-benzene.

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[1] Ethyl nitrite if present may be readily detected in the distillate by the brown colour produced on adding ferrous sulphate and strong sulphuric acid.

251. **Liqueurs** or **Cordials.**—Under these names are included a number of special and proprietary drinks consisting of grain spirit heavily sweetened and flavoured. They are sometimes brightly coloured; indigo, cochineal, turmeric, and gamboge being among the least objectionable agents employed, while aniline dyes, picric acid, and salts of copper are occasionally used. Sweetened gin is, strictly speaking, a *cordial* rather than a true *spirit*. Among the most popular liqueurs may be mentioned absinthe, curaçoa, maraschino, and noyeau. Robur, or "tea-spirit," which had a short-lived popularity due to extensive advertising, consisted of grain spirit, strongly sweetened and mixed with infusion of tea-leaves. Cherry-brandy, orange-bitters, and similar drinks are also of the nature of cordials. These preparations do not require detailed description.

252. ABSINTHE is a liqueur containing a somewhat variable proportion of real alcohol, and several units of volatile oils,—those of cinnamon, cloves, peppermint, anise, and angelica being frequently employed. Its characteristic constituent, however, is the oil of wormwood (*Artemisia absinthium*), to which the alleged deleterious properties of absinthe are probably attributable. In consequence of the presence of essential oils, absinthe becomes milky on addition of water. Some varieties of absinthe contain little or no sugar. The following table shows the amounts of alcohol and essential oils contained in four different brands of absinthe. The figures are due to Adrian, and are expressed in terms of a glass of 30 c.c. of the liqueur :—

	Absolute Alcohol.	Oil of Wormwood.	Total Essential Oils.
Ordinary absinthe . .	14·3 c.c.	·005 grammes	·030 grammes
"Demi-fine" „ . .	15·0 „	·010 „	·046 „
"Fine" „ . .	20·4 „	·010 „	·085 „
Swiss „ . .	24·2 „	·010 „	·085 „

A. Wynter Blyth states the average composition of the absinthe consumed in London (where its use is on the increase) to be—alcohol, 50·00; oil of wormwood 0·33; other essential oils, 2·52; sugar, 1·50; chlorophyll, traces; and water, 45·65 per cent.

Absinthe nearly always has a faintly acid reaction, which is probably due to acetic acid. It usually amounts to 1·5 grammes of acetic acid per litre. The green colour of absinthe ought to be due to chlorophyll, introduced from spinach, nettles, or parsley. A mixture of sulphate of indigo with picric acid or turmeric is not unfrequently employed, and salts of copper have also been used. Copper can be readily detected by diluting the liqueur and adding potassium ferrocyanide, which will occasion a brown colour. The vegetable colouring matters are perhaps best detected by their absorption-spectra. Picric acid may be recognised by diluting the liqueur with weak sulphuric acid, and shaking with ether, which will acquire a yellow colour and will dye silk yellow. Sulphuric acid and antimony compounds are stated by Gardun to have been added to absinthe.

The alcohol contained in absinthe may be determined by the ordinary process of distillation, the proportion of essential oils being insufficient to affect the density materially. For the determination of the essential oils, Baudrimont recommends that the distilled liquid should be diluted with twice its measure of water to cause the oils to separate, and then shaken with carbon disulphide. This being removed from the bottom by a tap, and allowed to evaporate spontaneously, leaves the essential oils.

253. **Noyeau** has a flavour which is sometimes due to hydrocyanic acid, and in other cases to oil of bitter-almonds, or to nitro-benzene (see Kirschwasser, par. 238).

254. **Tinctures.**—In medicine, various alcohol solutions are employed, their permanency rendering them very convenient. These solutions are called "tinctures" or "spirits." In some cases they are directed to be prepared with "Rectified Spirit, B.P." (sp. gr. 835 = 84 per cent. by weight of absolute alcohol). The tinctures and spirits of chloroform, ether, aconite, ferric chloride, ferric acetate, iodine, myrrh, nux vomica, camphor, ginger, &c., are made in this way. On the other hand, "Proof Spirit, B.P." (sp. gr. ·920) is directed to be used in making the tinctures of orange-peel, belladonna, cantharides, catechu, digitalis, ergot, opium, rhubarb, squills, &c.

There are in most cases good reasons for the choice of the above strengths of spirit, as experience shown them to be the best adapted for the solution of the active principles of the respective drugs.

As, in the preparation of the above tinctures, proof spirit is sometimes substituted for rectified spirit, and a mixture of equal measures of rectified spirit and water for proof spirit, it is sometimes required to ascertain the strength of the alcohol which has been employed.

255. Mere distillation is sufficient to separate the alcohol from the tinctures of aconite, arnica, belladonna, calumba, capsicum, catechu, jalap, nux vomica, opium, quinine, &c.; and the same is true of the tinctures of iodine, ferric acetate, &c., if they be first treated with soda in slight excess. On the other hand, the tinctures of benzoin, myrrh, ginger, camphor, rhubarb, &c., give distillates contaminated with essential oils or similar volatile matters in quantity sufficient to affect seriously the determination of the alcohol by the density. The same is true of the "aromatic spirit of ammonia" and tinctures prepared with it, with the additional objection that the distillate will contain ammonia, unless the alkaline reaction of the spirit be previously carefully neutralised by hydrochloric acid.

256. Spirits of chloroform, nitrous ether, and ether will of course yield distillates requiring special examination, or they can be examined directly. In the other tinctures to which the distillation process is not directly applicable, the alcohol may be determined in the following matter:—50 c.c. are taken and made up to 350 c.c. by addition of water. This usually causes a precipitation of the volatile oils or resinous matters, owing to their insolubility in water or very dilute alcohol. The liquid cannot be directly filtered, owing to the fine state of division in which the precipitate exists, but it may be clarified by adding a few drops of a strong solution of calcium chloride, followed by some sodium phosphate. The resultant precipitate of calcium phosphate entangles the oily and resinous matters. The liquid is now made up to 400 c.c., filtered through a dry filter, and 250 of the filtrate distilled at a low temperature, the distillate made up to 250 c.c. by addition of water, and its density observed. If the foregoing instructions be adhered to, the percentage of proof spirit corresponding to the density of the distillate, multiplied by 8, will be the percentage by volume of proof spirit contained in the tincture. The percentage of absolute alcohol by weight corresponding to this amount will be the percentage of alcohol contained in the spirit of the tincture.

257. This is the most convenient mode of expressing the alcoholic strength of tinctures, as it gives a figure which should approximate to the percentage by weight of absolute alcohol in the spirit used for making the tincture. Close accordance is not to be expected, for many of the drugs used contain water, and in other cases they sensibly increase the volume of the liquid.[1] In deciding on the strength of the alcohol employed in making the

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[1] Spirit of camphor has a volume equal to the sum of the measures of the camphor and alcohol used in preparing it.

tincture, the nature of the other ingredients should be carefully considered, and, when possible, a similar tincture should be made up with alcohol of known strength, and analysed in a similar manner to the sample.[1]

If from any cause, such as the appearance or smell of the distillate, there be doubt as to the freedom of the alcohol from matters liable to affect its gravity, the distillate may be examined by Monell's colorimetric method (see par. 160).

Occasionally tinctures are fraudulently prepared with methylated spirit. The substitution may be detected by the methods described in par. 133 *et seq.*

258. DEPOSITS FROM TINCTURES.—Many tinctures have a tendency to give deposits on keeping, and it is evidently important to know whether the active principles of the tinctures have a

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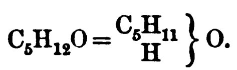
[1] A good example of the mode of examining a tincture is afforded by the "compound tincture of camphor," B.P., a remedy largely employed by the medical profession, and commonly known to the public by the obsolete name of "Paregoric Elixir." This preparation consists of a solution of 40 grains each of opium and benzoic acid, 30 of camphor, and half a fluid drachm of oil of anise, dissolved in proof spirit, and diluted with the same to one pint. The spirit being the most costly ingredient, there is a strong inducement to the vendor to reduce its amount, a practice which necessitates the omission of a portion of some of the other ingredients. On diluting genuine compound tincture of camphor the major part of the oil of anise is precipitated, and if the diluted liquid be then treated with calcium chloride and excess of sodium phosphate, filtered, rendered distinctly alkaline, and distilled, the alcohol is obtained in a state of approximate purity. The small quantity of camphor present in the original tincture passes over with the spirit, and modifies the density of the product to a slight extent; the difference is unimportant. In the case of compound tincture of camphor, the treatment with calcium chloride is not strictly necessary, as the proportion of oil of anise is very small, but carbonate of sodium should be added to fix the benzoic acid. The "extract" from the distillation should be concentrated to a small bulk, and strong hydrochloric acid added in excess. This should cause a precipitation of benzoic acid, and on shaking the liquid with ether, separating the upper layer, and evaporating off the ether by a current of dry air, the benzoic acid is obtained in a state of approximate purity and in a state fit for weighing. After weighing it may be moistened with ferric chloride, which will produce a deep red colour if the original preparation contained opium. Sometimes the benzoic acid is wholly omitted from the compound tincture of camphor. The same remark applies to the oil of anise, more than traces of which cannot be present if the tincture remains clear when diluted with three or four times its measure of water. The proportion of opium present in compound tincture of camphor can be judged of by the depth of red colour produced when the sample (previously diluted with water or proof spirit) is treated with ferric chloride. By comparing the tint obtained with that given by a similar tincture of known quality, a fair criterion of the proportion of opium may be obtained.

tendency to pass into the deposited matter. The subject has been investigated by R. A. Cripps (*Pharm. Jour.* [3] xiv., 483), whose results may be epitomised as follows:—

The deposits from the tinctures of calumba, cardamoms, gentian, ipecacuanha, and lobelia were free from the active principles of the drugs. The deposit from tincture of rhubarb contained a small proportion of chrysophanic acid, but was not tested for cathartic acid. Tincture of cinchona gives a deposit containing a notable but variable proportion of alkaloids, and the deposit from the compound tincture is of the same character, in addition to containing cochineal. Tincture of quinine is made by dissolving sulphate of quinine in tincture of orange-peel, and gives a deposit containing much calcium sulphate. On exposure to a low temperature, however, crystals of quinine sulphate are apt to form. The hydrochloride or hydrobromide of quinine would yield a tincture preferable to that made from the sulphate.

259. AMYL ALCOHOL.

Amylic Hydrate· Potato-spirit.



$C_5H_{12}O = \left.\begin{matrix} C_5H_{11} \\ H \end{matrix}\right\} O.$

—Several amylic alcohols are known, differing somewhat in their physical and chemical properties. Normal amyl alcohol boils at 137° C. Iso-amyl alcohol boils at 128° to 132° C., and has a density of ·8148 at 14° C. This is the variety of amyl hydrate produced by fermentation, and therefore present in fusel oil, and all subsequent statements respecting amyl alcohol have reference to the iso-variety.[1]

The preparation of amylic alcohol from fusel oil is described in par. 267.

Pure amylic alcohol is a colourless liquid of strong peculiar odour and acrid burning taste. Dropped on paper it produces an oily mark which disappears slowly.

One part of pure amylic alcohol dissolves in 39 parts of water at 15°·5 C., forming a liquid of ·998 specific gravity. One part of water dissolves in 11·6 parts of amylic alcohol, forming a clear liquid of ·835 specific gravity.

Amylic alcohol is miscible in all proportions with ethyl alcohol, ether, chloroform, carbon disulphide, benzene, petroleum ether, and fixed and volatile oils; and is itself a solvent for sulphur, phosphorus, iodine, camphor, and many alkaloids and resins.

Amylic alcohol dissolves in all proportions in glacial acetic acid diluted with an equal bulk of water, and may thus be separated from neutral amylic ethers (*e.g.*, acetate, valerate, and pelargonate of amyl) which are not soluble in acetic acid.

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[1] Further information respecting the alcohols of fusel oil will be found in par. 265.

Commercial amylic alcohol is liable to contain traces of an alkaloidal body which may be removed by agitation with dilute acid, but the presence of which renders the liquid unfit for use as a solvent for alkaloids, &c., in toxicological investigations.

260. Amylic alcohol is very injurious. A few drops will produce all the intoxicating effects of a large quantity of ethyl alcohol, with giddiness, nausea, and other unpleasant symptoms.[1] In larger doses it proves fatal. To its presence in new whisky the injurious effects of that spirit are attributable. On keeping the spirit, most of the amyl alcohol becomes more or less oxidised or converted into comparatively harmless ethers, and the injurious effects are less evident.

261. DETECTION OF AMYLIC ALCOHOL.

a. When amylic alcohol warmed with 1½ to 2 times its volume of strong sulphuric acid, amyl-sulphuric acid, C_5H_{11},HSO_4, is formed, with production of a red colour. Amyl-sulphuric acid is viscid, soluble in water and alcohol, and decomposed by distillation. In presence of sugar and other fixed substances this test is very fallacious, but if applied to a product of distillation, especially if boiling between 120° and 135° C., the production of even a faint red colour is strong presumptive evidence of the presence of amyl alcohol.

b. When amylic alcohol is heated with an acetate and strong sulphuric acid, amyl acetate is formed (see par. 349), which when perfectly pure has the odour of the jargonelle pear. In presence of $\frac{1}{30}$th part of ethyl alcohol, the product smells of the bergamot pear.

c. When amylic alcohol is heated with an oxidising agent, *e.g.*, sulphuric acid and bichromate of potassium, an apple-like odour of valeric aldehyde, $C_5H_{10}O$, is first produced, followed by the strong and peculiar smell of valeric acid, $C_5H_{10}O_2$. In presence of much ethyl alcohol, the smell of the resultant acetic acid quite overpowers that of the valeric acid.

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[1] According to the experiments of Rabuteau, amylic alcohol produces intoxicating effects of a similar kind to those due to ethyl alcohol, but 15 times as intense. (The effects of butyl alcohol were only 5 times as intense.) The researches of other observers have shown that the physiological effect of the alcohols increases with the number of carbon atoms. Brockhaus has recently personally investigated the effects of propyl, butyl, and amyl alcohols on the system. He found the disagreeable symptoms to increase with the molecular weight of the alcohols, and amyl alcohol itself proved to be a very violent poison. He concluded that the impurities of potato-brandy had a much more active influence on the human organism than was exerted by ethyl alcohol.

262. THE DETERMINATION OF AMYL ALCOHOL may be approximately effected by oxidising it to valeric acid by dilute chromic acid mixture as described in par. 295. In the absence of other acid-yielding substances, the valeric acid may be determined by titration, but otherwise the method described in the section on the "Homologues of Acetic Acid" must be resorted to.

The determination of amyl alcohol in spirituous liquids is based on the above principles (see par. 273).

263. THE SEPARATION OF AMYL ALCOHOL from moderate quantities of ethyl alcohol is fully described under fusel oil (see par. 268). From butyl alcohol and valeric aldehyde (boiling at 93° C.), amylic alcohol may be approximately separated by fractional distillation (see par. 267). From neutral amylic ethers, amylic alcohol may be separated by agitation with glacial acetic acid diluted with an equal bulk of water,—a mixture in which the ethers are insoluble.

264. Fusel Oil.

In the alcoholic fermentation of potatoes, corn, and the marc of grapes, there are always formed,—and especially when the fermentation is conducted in an alkaline, or but slightly acid, liquid,—in addition to common alcohol, various oily bodies of higher boiling points than alcohol, and which are, therefore, found in the last portions of the distillate obtained in the process of rectification. These liquids consist chiefly of alcohols of the series $C_nH_{2n+2}O$, and together constitute "fusel" or "fousel oil."

265. Potato fusel oil sometimes consists almost entirely of ethylic and amylic alcohols,[1] the latter forming the larger proportion. Fusel oil from other sources often contains propylic, butylic, and hexylic alcohols, and various aldehydes and ethers are frequently present.

The following table shows the formula, densities, and boiling

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[1] The following proportions of various alcohols, &c., were obtained by Rabuteau (*Compt. Rend.*, lxxxvii. 501) from 1 litre of potato fusel oil :—

Iso-propyl alcohol,	150 c.c.
Propyl alcohol,	30 ,,
Iso-butyl alcohol,	50 ,,
Normal butyl alcohol,	65 ,,
Methyl-propyl carbinol,	60 ,,
Iso-amyl alcohol,	275 ,,
Products boiling above 132° and retaining amyl alcohol,	170 ,,
Water,	125 ,,
Ethyl alcohol, aldehyde, and ethyl acetate,	75 ,,

Trimethyl-carbinol also appears to have been present. No mention is made of the presence of amylic ethers.

points of the various alcohols which occur, or are supposed to occur, in fusel oil:—

		Density.	Boiling Point °C.
C_2H_6O	Ethyl Alcohol, $CH_3.CH_2.OH$, ... (Methyl-carbinol.)	·7938	78·4
C_3H_8O Propyl alcohols	1. Normal Propyl Alcohol, $CH_3.CH_2.CH_2.OH$, . . . (Ethyl-carbinol.)	8066	97·4
	2. Iso- or secondary Propyl Alcohol, $(CH_3)_2:CH.OH$, . . (Dimethyl-carbinol.)	·787	82·8
$C_4H_{10}O$ Butyl alcohols	1. α-Normal-primary[1] Butyl Alcohol, $CH_3.CH_2.CH_2.CH_2.OH$, . (Propyl-carbinol.)	·813	117·0
	1. β-Iso-primary Butyl Alcohol, $(CH_3)_2:CH.CH_2.OH$, . . (Iso-propyl-carbinol.)	·799	108·4
	2. Tertiary[1] Butyl Alcohol, $(CH_3)_3:C.OH$, . . . (Trimethyl-carbinol.)	melts at 25°	82·5
$C_5H_{12}O$ Pentyl alcohols	1. α-Normal-primary Amyl Alcohol $CH_3.CH_2.CH_2.CH_2.CH_2.OH$, (Butyl-carbinol.)	·820	137
	1. β-Iso-primary Amyl Alcohol, $(CH_3)_2:CH.CH_2.CH_2.OH$, . (Isobutyl-carbinol.)	·814	131
	1. γ-Iso-primary Amyl Alcohol, (Secondary Butyl carbinol.) $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}:CH.CH_2.OH$, . .	·813	128
	2. Methyl-propyl carbinol, $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}:CH.OH$, . . .	·816	120
$C_6H_{14}O$	Iso-primary Hexyl Alcohol, $(CH_3)_2:CH.CH_2.CH_2.CH_2.OH$, .	...	148–154
$C_7H_{16}O$	Iso-primary Heptyl Alcohol, $(CH_3)_2:CH.CH_2.CH_2.CH_2.CH_2.OH$,	...	155–160

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[1] The classification of alcohols as primary, secondary, and tertiary is based on their supposed constitution. In the *primary* alcohols the hydroxyl group is always connected with the group CH_2.; thus, $CH_2.OH$. In the *secondary* alcohols it is linked to CH., and in the *tertiary* alcohols to C.. The boiling points of the primary are higher than those of the secondary, and these again boil at a higher temperature than the corresponding tertiary alcohols. On oxidation by chromic acid mixture (par. 295), the primary alcohols yield *aldehydes* containing the same number of carbon atoms, and these by further oxidation are converted into acids of the acetic series containing the same number of carbon atoms as the original alcohols; the secondary alcohols yield *ketones* containing the same number of carbon atoms, but which on further oxidation furnish acids of the acetic series containing fewer carbon atoms than the original alcohols; and, lastly, the tertiary alcohols do not under any circumstances yield acids containing the same number of carbon atoms.

The following method enables alcohols of different series to be more readily recognised. The alcohol is heated with hydriodic acid, and thus converted into the corresponding iodide. This is dried and added to an equal weight of dry argentic nitrite, previously mixed with its own volume of dry sand. The flask is heated over a small flame, and when action is over the mixture is distilled into a test-tube, where it is shaken with three times its measure of strong potash solution containing some potassium nitrite. Dilute sulphuric acid is then added drop by drop till the reaction is acid. If a *primary* alcohol has been operated on the liquid will assume an intense red colour; if a *secondary*, it becomes dark blue; while the product from a *tertiary* alcohol remains colourless. The test succeeds with as little as half a gramme of the alcoholic iodide.

266. The researches of Pasteur, Le Bel, and Ley have proved that the amylic alcohol of fusel oil really consists of a mixture of two iso-primary amyl alcohols of nearly identical boiling points and specific gravities. One of these (iso-butyl carbinol) is optically inactive, but the other presents the unique property (for an alcohol) of rotating the plane of a polarised ray of light to the left. On oxidation they are acted on with very different facilities, but both furnish valeric aldehydes, which on further oxidation are converted into valeric acids. The acid derived from the optically active alcohol is also optically active, but *dextro-rotatory*, and it forms a gummy barium salt, that from the inactive acid being crystalline. The quinine salts exhibit the same difference.

267. Amylic alcohol may be separated from fusel oil in a state of approximate purity, by agitating the liquid with strong brine, separating and distilling the oily layer, and collecting separately the portion which passes over between 125° and 140° C. The fraction which distils between 105° and 120° C. consists almost entirely of iso-butyl alcohol.

The amyl alcohol obtained in the above manner may be further purified by agitating it with hot milk of lime, drying with chloride of calcium, rectifying, and collecting separately the portion which distils between 128° and 132° C.

For the mode of separating amylic alcohol from the neutral ethers and aldehydes of fusel oil, see par. 263.

268. Fusel oil may be imported into England free of duty if it contain less than 15 per cent. of proof spirit. It is tested by the Excise by shaking it with an equal volume of water to remove the spirit, and then ascertaining the amount of alcohol contained in the aqueous liquid by taking its specific gravity. The test gives erroneous results, as fusel oil is a mixture of various alcohols, of which only amylic is approximately insoluble in water. As an improvement on this test, G. L. Ulex (*Neues Jahrb. der Pharm.*, xxxix. 333) recommends the following, based on the low temperature at which ethyl alcohol distils:—100 c.c. of the sample are heated in a retort till 5 c.c. have passed over; the distillate is shaken with an equal volume of a saturated solution of common salt, and the mixture allowed to stand. If the fusel oil which separates amounts to one-half of the distillate or more, the sample is sure to contain less than 15 per cent. of spirit, and is free from any fraudulent admixture with the same. If less fusel oil, or none at all, separate, the presence of 15 per cent. of the spirit may be safely assumed. In the latter case, the quantity of the adulterant may be determined by shaking a known measure of the sample with an equal bulk of a saturated solution of common salt (in which propyl and

butyl alcohols are much less soluble than in water), allowing the aqueous liquid to settle out, distilling it, and estimating the contained alcohol by noting the volume and density of the distillate.

269. The author has proved the accuracy of another method of approximately separating amylic from ethylic alcohol, which is to agitate the sample in a graduated tube with an equal volume of benzene or petroleum spirit, subsequently adding sufficient water to cause the benzene to separate. The increase in the volume of the benzene indicates with approximate accuracy the amount of amylic alcohol in the sample under examination.

270. Detection of Amylic Alcohol in Spirituous Liquids.

Amylic alcohol occurs to a greater or less extent in many varieties of commercial alcohol, especially those obtained by the fermentation of grain or potatoes. To its presence in recently manufactured whisky the deleterious effects of the raw spirit are attributable. On keeping, the amylic alcohol is more or less destroyed by oxidation and conversion into comparatively harmless ethers.

The actual proportion of amylic alcohol present in different varieties of whisky is very uncertain, but few accurate experiments having been made. According to Dupré, a sample of Scotch whisky contained 0·19 of amylic alcohol for 100 of ethylic alcohol. A sample of "Cape Smoke" contained 0·24, and of "Common Samshoe" 0·18 of amyl alcohol per 100 of ethyl alcohol.

The alleged adulteration of whisky with fusel oil is probably based on an error, though it is quite possible that it has occurred in exceptional cases. The natural variation in the proportion of amylic alcohol contained in spirit is very considerable, being materially affected by the mode of distillation, in addition to the causes previously mentioned.

271. Of the many methods of detecting amylic in spirituous liquids, comparatively few have any value. The following have all been tried by the author, and verified to the extent stated:—

a. A useful rough test is to pour the sample of spirit on filter paper contained in a plate or flat basin, allowing it to evaporate spontaneously, or by the application of a very gentle heat. In the last portions the smell of fusel oil is often distinctly recognisable, especially if the liquid be warmed. A sample of gin to which $\frac{1}{2000}$ of amyl alcohol had been added was found by the author to respond to this test.

b. Another useful indication is afforded by dissolving 1 gramme of caustic potash in 150 c.c. of the spirit, evaporating the liquid slowly down to 15 c.c., and then mixing it with an equal measure

(15 c.c.) of dilute sulphuric acid, when the liquid will exhale an odour which is often characteristic of the origin of the spirit, and indicative of its source in raw grain, malt, potatoes, rye, arrack, &c. The odour produced is often very disgusting.

c. A valuable means of concentrating the fusel oil is to distil off the greater part of the alcohol at as low a temperature as possible. In the residual liquid, especially while it is warm, the fusel oil may often be detected by the smell. The residual liquid is mixed with an equal measure of ether, and then well shaken. If the ethereal layer do not separate spontaneously, an equal measure of water should be added. The ethereal layer is separated, and allowed to evaporate spontaneously. In the residue, amylic alcohol may be recognised by its smell and chemical characters. Petroleum ether may be advantageously substituted for the ether, as, owing to its slight solubility in alcohol, it may often be applied to the original liquid.

By pouring the mixed liquid through a wet filter, the author found he could get rid of the ordinary alcohol and water, while the amylic alcohol was retained by the ether, which rapidly evaporated and left the fusel oil in a state readily recognisable by the smell. The amylic alcohol in a gin, to which $\frac{1}{2000}$ had been purposely added, was readily recognised by the author in this manner. If desired the residue can be further examined by one of the following tests:—

d. L. Marquardt dilutes 40 c.c. of the spirit with sufficient water to bring the density to about ·980, and then agitates the liquid with 15 c.c. of pure chloroform. The chloroform is allowed to settle, separated, and, after shaking with an equal measure of water, is allowed to evaporate spontaneously. The residue is treated with a little water and one or two drops of sulphuric acid, and sufficient solution of potassium permanganate is then added to cause the mixture to remain red after standing for 24 hours in a closed tube. Shortly after adding the permanganate, the smell of valeric aldehyde will be observed, but after standing only the odour of valeric acid is distinguishable. This can be recognised even when the original residue is almost odourless, and the smell is not masked by the presence of essential oils, &c.

e. Many samples of alcohol containing fusel oil to the extent of 0·1 per cent. respond to the following test, which depends on the existence of furfuraldehyde in the sample:—10 c.c. of the spirit are mixed with 10 drops of colourless aniline, and 2 or 3 drops of sulphuric acid, when a fine red colour will be produced. The test is still more delicate if the residue of a chloroform or ether extraction of the spirit be used for the experiment.

272. THE DETERMINATION OF FUSEL OIL IN SPIRITS cannot be effected very accurately, as it is present in very small proportion and is not a definite substance, being a variable mixture of amylic, butylic, and other alcohols, various amylic ethers, &c. Most methods aiming at the actual estimation of the fusel oil are based on the determination of the amyl alcohol, which is its leading constituent.

273. The following process, due to L. Marquardt (*Ber. Chem. Ges.*, xv. 1661, and *Jour. Soc. Chem. Ind.*, i. 331, 377), is based on the extraction of the amylic alcohol by chloroform, its oxidation to valeric acid, the conversion of the latter into barium valerate, and the estimation of the barium thus combined:—150 grammes of the sample are diluted with water to a density of about ·980 and agitated with 50 c.c. of pure chloroform [1] for a quarter of an hour. The aqueous layer is separated and shaken with another 50 c.c. of chloroform, and subsequently treated a third time. The 150 c.c. of chloroform, containing in solution the amylic alcohol of the spirit, is treated in a strong flask or bottle with 2 grammes of sulphuric acid and a solution of 5 grammes of potassium bichromate in 30 c.c. of water. The flask is then closed and kept at a temperature of 85° C., with frequent agitation, for six hours. The liquid is then distilled till all but 20 c.c. have passed over, when 80 c.c. of water is added to the residue and the distillation repeated till only 5 c.c. remains in the flask. The distillates are digested for half an hour with barium carbonate, in a flask furnished with an inverted condenser, after which the chloroform is distilled off and the aqueous liquid evaporated to a volume of 5 c.c. The solution is then filtered from the excess of barium carbonate, and the filtrate evaporated to dryness at 100.° The residue ("A") is weighed, dissolved in water, and the solution diluted to 100 c.c. 50 c.c. measure is acidulated with nitric acid and precipitated by silver nitrate, the resultant chloride of silver being collected, weighed, and calculated into its equivalent of chlorine (143·5 of $AgCl = 35{\cdot}5$ of Cl). The remaining 50 c.c. is precipitated with dilute sulphuric acid, the barium sulphate being collected and weighed. The weight found is calculated into its equivalent of

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[1] Chloroform prepared from chloral is to be preferred, as the ordinary kind, though it may not colour sulphuric acid, is apt to contain impurities which yield valeric acid and other volatile fatty acids by oxidation. For its purification, 220 c.c. are heated in a well-closed bottle with 3½ grammes of potassium bichromate, 1·4 grammes of sulphuric acid, and a small quantity of water. The mixture is kept at 85° C. for six hours and frequently shaken. The chloroform is then distilled off, and shaken with water and barium carbonate. The mixture is heated for half an hour in a flask fitted with an inverted condenser, when the chloroform is again distilled.

barium (233 of $BaSO_4 = 137$ of Ba). The sum of the weights of the barium and chlorine found, subtracted from that of the residue A, gives the weight of the valeric radicle contained therein, and this multiplied by the factor 0·871 gives the weight of amylic alcohol in the 150 grammes of spirit employed for the operation. The errors produced by the presence of substances in the fusel oil other than amylic alcohol tend to compensate each other, and hence the results are very fairly accurate. Marquardt obtained 1·02 grammes of fusel oil for 1000 grammes of spirit, against 1·00 gramme added.

274. *b.* When the proportion of fusel oil is considerable, the amount may be approximately ascertained by distilling 500 or 1000 c.c. of the spirit to 135° C. in a flask furnished with a fractionating tube (see par. 35). When the thermometer rises to 98° the receiver is changed, and the portion distilling between that temperature and 110° collected separately and again fractionally distilled. The last portion so obtained is added to the part of the first distillate coming over between 110° and 135° C. These united distillates are set aside; after the first hour or two, if no aqueous layer separates at the bottom, ¼th of the volume of water is added, and the whole agitated. After twelve hours, the aqueous layer is separated with a pipette and the residual fusel oil measured or weighed. This process aims at the direct determination of the fusel oil as such, instead of the estimation of any leading constituent. Probably the method might be advantageously modified by agitating the fusel oil distillate in a graduated tube with an equal volume of benzene or petroleum spirit, and estimating the amount of fusel oil from the increase in the bulk of the upper layer.

NEUTRAL ALCOHOLIC DERIVATIVES.

275. Among the neutral derivatives of the alcohols are included a number of important bodies, of which chloroform, ether, compound ethers, and aldehyde are prominent examples.

As a rule, the neutral derivatives of the alcohols are volatile ethereal liquids, but important exceptions exist to this generalisation. The bodies of this division employed in commerce are of too varied a nature to admit of general description. The more important of them are fully discussed under special sections devoted to them.

276. ETHER.

Ethylic Ether.[1] Ethyl Oxide.

French—Ether. *German*—Aether.

$$C_4H_{10}O = \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O = C\left\{\begin{matrix} CH_3 \\ H \\ H \\ O.C_2H_5. \end{matrix}\right.$$

When used as a proper name the term "ether" always signifies ethylic ether. When employed generically the word ether has a far wider signification (see par. 287).

Ether can be obtained by a variation of reactions, but is always manufactured in practice by distilling alcohol with strong sulphuric acid.[1] The reaction consists first in the production of ethylsulphuric acid (sulpho-vinic acid) $C_2H_5HSO_4$, and this product at a higher temperature (130° C.) acts on a second molecule of alcohol with formation of ether.

1. $C_2H_5HO + H_2SO_4 = C_2H_5,HSO_4 + H_2O$; and
2. $C_2H_5HSO_4 + C_2H_5HO = (C_2H_5)_2O + H_2SO_4$.

It is thus evident that sulphuric acid is reproduced. Theoretically, therefore, a limited quantity of sulphuric acid is capable of converting a much larger quantity of alcohol into ether. Advantage is taken of this fact in practice, but the formation of secondary products ultimately puts a stop to the process. The first distillate contains (besides ether) alcohol, water, sulphurous and acetic acids, oil of wine, &c. By addition of water the alcohol may be eliminated, the ether forming a separate layer on the surface. The acids and water may be got rid of by agitation with potassium carbonate, and the ether obtained pure by redistillation.[1]

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[1] In reference to this mode of preparation, ether was formerly called "sulphuric ether."

277. Ether is a highly volatile, colourless, limpid liquid, of penetrating agreeable odour, and pungent sweetish taste. When pure, it boils at 35° C., and has a density according to Mendelejeff of 0·7174 at 15° C., or 0·7364 at 0° C. It solidifies at −129° C. to a white crystalline mass, which liquefies at −117·4° C.

Ether is sparingly soluble in water, and still less so in glycerin, the solutions having a neutral reaction. With alcohol, chloroform, benzene, petroleum spirit, fixed and volatile oils, ether is miscible in all proportions.

Ether dissolves resins, fats; many alkaloids; phosphorus, bromine, and iodine; ferric, mercuric and auric chlorides; and mercuric (but not mercurous) iodide.

In the air, ether oxidises very slowly to acetic acid. Both the liquid and vapour are very combustible, burning with a white luminous flame.

278. Commercial Ether.

Commercial Ether frequently contains water (1 part of water dissolves in 35 of ether), and very considerable quantities of alcohol.

"Ether" B.P., is described as having a specific gravity of 0·735, and containing not less than 92 per cent. by volume of real ether.

The "Ether" of the German Pharmacopœia has a specific gravity of 0·724 to 0·728, and boils at 34° to 36° C.

The "Ether" of the French Codex has a density of 0·720 to 0·725 at 15° C.

The "Ether" of the United States Pharmacopœia has a density of about 0·750, and consists of 74 per cent. of real ether, and 26 per cent. of alcohol containing a little water. "Æther fortior,"

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[1] In the arrangement employed by Dr Squibb, the vapours of ether and unchanged alcohol are first washed by a solution of caustic potash maintained at a temperature above the boiling point of alcohol, the latter liquid is then condensed in a worm kept at a suitable temperature, and runs back into the still, while the ether vapour retaining about 4 per cent. of alcohol is condensed in a well-cooled arrangement. 360 lbs. of concentrated sulphuric acid suffice to etherify 120 barrels of clean spirit, and then has to be changed chiefly because the impurities of the spirit render the mixture dark and tarry and liable to froth in the still (*Ephemeris*, ii. 590).

U.S.P., is stated to have a density not exceeding 0·725 at 15° C., and to boil at 37° C.

From these characters it is evident that the presence of water or alcohol in ether tends to raise the boiling point and increase the density of the liquid.

279. The following table by Dr Squibb (*Ephemeris*, ii., 598), shows the density of various mixtures of ether of 0·71890 specific gravity with alcohol of ·82016 specific gravity (=90·94% by weight of absolute alcohol); the densities of both liquids being taken at 60° F. (=15·5° C.), and compared with water at the same temperature taken as unity :—

Percentage of Ether by Weight.	Specific Gravity.	Percentage of Ether by Weight.	Specific Gravity.	Percentage of Ether by Weight.	Specific Gravity.
99	·72021	89	·73298	79	·74495
98	·72152	88	·73428	78	·74612
97	·72284	87	·73547	77	·74729
96	·72416	86	·73666	76	·74846
95	·72541	85	·73785	75	·74975
94	·72666	84	·73904	74	·75104
93	·72792	83	·74022	73	·75233
92	·72918	82	·74141	72	·75362
91	·73043	81	·74260	71	·75492
90	·73168	80	·74378	70	·75623

280. Absolute ether forms a clear mixture with any proportion of oil of copaiba. If it contain alcohol or water it forms an emulsion when shaken with a considerable proportion of the oil. Anhydrous ether also forms a perfectly clear mixture with an equal bulk of carbon disulphide; but if the smallest quantity of water be present the mixture is milky.

Gallotannic acid (tannin) is not affected by perfectly anhydrous ether, but it deliquesces to a syrup if a small proportion of alcohol or water be present.

281. The most delicate test for the presence of alcohol in ether is that of Lieben, founded on the formation of iodoform by alcohol but not by ether. The method of applying the test is described in par. 151, *c.* Very careful purification is necessary to obtain ether which does not respond to this test, and mere keeping in presence of moisture generates traces of alcohol sufficient to produce the reaction.

282. Several chemists have pointed out that crystallised fuchsine (acetate of rosaniline [1]) is insoluble in pure anhydrous ether

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[1] The hydrochloride of aniline is not suitable for this test.

or chloroform, but that it imparts more or less colour to these liquids when alcohol or water is present.

When the sample is well agitated with dry chloride of calcium to remove alcohol and water, it loses the power of dissolving fuchsine, becoming tinged only very faintly when shaken with the dye.

To employ the above facts for the determination of small quantities of alcohol in ether, the author operates in the following manner (*Analyst*, ii. 97):—A minute quantity of powdered fuchsine is placed in a narrow test-tube, 10 c.c. of the ether added, the tube corked, and the whole agitated. If the ether be pure and anhydrous, the coloration of the liquid will be almost *nil.* If the coloration be considerable, 10 c.c. of ether which has been treated with chloride of calcium is placed in another tube of the same bore as the first, adding fuchsine as before. $\frac{1}{10}$th c.c. of alcohol is then added to it from a finely-divided burette, and the whole is shaken. If this quantity of alcohol be insufficient to produce a coloration of the liquid equal to that of the sample to be tested, a further addition of alcohol must be made until the liquids have the same depth of colour. The tint is best observed by holding the two tubes side by side in front of a window and looking through them transversely. The use of a piece of wet filter-paper behind them facilitates the observation. It is well to permit the alcohol to drop right into the ether, and not allow it to run down the sides of the tube, as in the latter case it will dissolve any adherent particles of fuchsine, forming a solution which will be precipitated on mixing with the ether. For a similar reason it is not convenient to dilute the sample with pure ether, so as to reduce the colour to that of a standard tint. In practice, each 0·1 c.c. of alcohol added from the burette may be considered as indicating 1 per cent. of impurity in the sample. Of course this assumption is not strictly correct, but the error introduced is insignificant when the percentage of alcohol is small. The method is very suitable for small proportions of alcohol, but becomes difficult to apply when the latter exceeds 5 per cent. of the sample, owing to the intensity of the colour. The results are within ¼ per cent. of the truth. Occasionally the tints of the two liquids are not readily comparable, but on placing the tubes for a few minutes in cold water, this difficulty is overcome. It has been pointed out by E. R. Squibb, that the fuchsine test fails to detect a proportion of alcohol below 0·2 per cent.; but allows the recognition of very minute traces of water in ether.

283. Ether free from alcohol is soluble in eleven times its measure of water. Agitation with water extracts any alcohol it

may contain, and thus diminishes the volume of the ether. The method appears very unpromising in presence of much alcohol, but with certain precautions, it is possessed of considerable accuracy. The following are the details of the procedure the author has found preferable (*Analyst*, ii. 98) :—A small quantity of fuchsine is placed in a separator or Mohr's burette, which is then filled with water and a small proportion of ether, and the whole agitated. By this means a coloured etherised water is obtained, in which ether is quite insoluble, while alcohol readily dissolves. 10 c.c. measure of the etherised water is run into a glass tube holding about 25 c.c., and having divisions of $\frac{1}{10}$ c.c., 10 c.c. of the sample of ether are next added, the tube corked, and the whole well shaken. On the ether rising to the surface, its volume can be easily read off. Any reduction in its volume is due to admixture of alcohol. Thus each 0·1 c.c. lost represents 1 per cent. of alcohol. If the proportion of alcohol in the sample does not exceed 20 per cent., the ether will be colourless, and the result of the experiment will be correct; but if the proportion of alcohol be much above 20 per cent., the layer of ether will be coloured, and the result below the truth. The absence of colour, therefore, in the ethereal layer, indicates the accuracy of the experiment. If the ether be coloured, an accurate result can still be obtained by adding 5 c.c. of anhydrous ether, and again agitating. It is better, however, to dilute a fresh portion of the sample with an equal bulk of pure ether, and use the diluted sample instead of the original. By proceeding in this manner the proportion of alcohol in mixtures of that liquid with ether can be ascertained within 1 or 2 per cent. with great facility. The process has been verified up to 60 per cent. of alcohol.

In all cases the proportion of alcohol must be deduced from the reduction in the volume of the ether, and not from the increase in that of the aqueous liquid. Care must be taken to prevent any volatilisation of the ether.

The above method of agitation with etherised water is far more rapid and generally preferable to the shaking with glycerin sometimes recommended.

284. The presence of more objectionable impurities in ether is indicated when at least 10 c.c. of the sample is allowed to evaporate spontaneously on filter-paper contained in a flat dish, and the odour of the "tailings" is carefully observed.

Some specimens of commercial ether liberate iodine from potassium iodide, a reaction which is not improbably due to the presence of traces of ethyl nitrite.

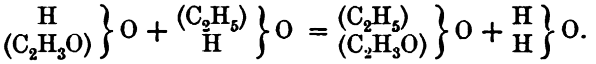
285. **Methylic Ether.** $(CH_3)_2O$.—When methyl alcohol is

heated with sulphuric acid it yields methylic ether, which is a gas condensible only at a very low temperature, and the solution of which in ordinary ether possesses remarkable anæsthetic properties. Owing to the extreme volatility of methylic ether, ether made from methylated spirit would be practically pure ethylic ether, were it not for the presence in it of other constituents of wood spirit. Ether prepared from methylated spirit is known as "methylated ether."

286. "Spirit of Ether," B.P., is a solution of about 28 parts of real ether in 72 of rectified spirit. The corresponding preparations of the German and United States Pharmacopœias contain respectively 23½ and 22 per cent. of ether.

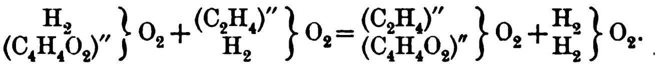
287. COMPOUND ETHERS.

This term is applied to the products obtained when acids react on alcohols with elimination of water, as in the cases represented by the following formulæ:—



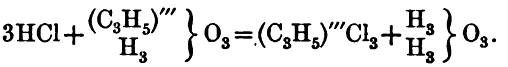
$$\left.\begin{matrix} H \\ (C_2H_3O) \end{matrix}\right\} O + \left.\begin{matrix} (C_2H_5) \\ H \end{matrix}\right\} O = \left.\begin{matrix} (C_2H_5) \\ (C_2H_3O) \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \end{matrix}\right\} O.$$

Acetic acid. Ethyl alcohol. Acetate of ethyl.



$$\left.\begin{matrix} H_2 \\ (C_4H_4O_2)'' \end{matrix}\right\} O_2 + \left.\begin{matrix} (C_2H_4)'' \\ H_2 \end{matrix}\right\} O_2 = \left.\begin{matrix} (C_2H_4)'' \\ (C_4H_4O_2)'' \end{matrix}\right\} O_2 + \left.\begin{matrix} H_2 \\ H_2 \end{matrix}\right\} O_2.$$

Succinic acid. Glycol. Ethylene succinate.



$$3HCl + \left.\begin{matrix} (C_3H_5)''' \\ H_3 \end{matrix}\right\} O_3 = (C_3H_5)'''Cl_3 + \left.\begin{matrix} H_3 \\ H_3 \end{matrix}\right\} O_3.$$

Hydrochloric acid. Glycerin. Trichloride of glycyl.

288. Ethers can be produced in various ways, but the following general methods may be specially mentioned:—

1. By the action of the concentrated acid upon the anhydrous or concentrated alcohol containing the radicle of which an ether is desired.

2. By distilling the alcohol with strong sulphuric acid and a salt of the acid the radicle of which is to be introduced into the ether.

3. By dissolving the acid in the alcohol and passing hydrochloric acid gas into the liquid.

4. By reaction between the iodide of the alcohol radicle the ether of which is required and the silver salt of the acid.

In many respects the ethers may be regarded as true salts of the alcohol radicles, but they rarely react directly with the ordinary tests for the contained acid radicles.

289. As a class, the ethers are mostly volatile solids or liquids

having little solubility in water, but miscible in all proportions with alcohol and ether. They are frequently split up into the corresponding acids and alcohols by distillation with water (and especially by high-pressure steam), and yield the alcohol and an alkaline salt when treated with caustic alkali.

290. The following is a tabular list of the chief ethers of *monatomic* alcohol-radicles of which practical application is made :[1]—

Name.	Formula.	Boiling Point °C.	Specific Gravity		Other Characters and Applications.
			at 0° C.	at 15° to 18° C.	
Methyl acetate, .	$CH_3,C_2H_3O_2$	56·3	·867	...	Readily soluble in water; present in wood naphtha.
" salicylate, .	$CH_3,C_7H_5O_3$	222·	...	1·18	See vol. ii.
" chloride, .	CH_3,Cl	–23·	...	...	Gaseous at ordinary temperatures; used for refrigerating and for producing methyl-aniline dyes.
" iodide . .	CH_3,I	42·5	...	2·23	Turns brown in the light. Aniline dyes.
Ethyl formate, . .	C_2H_5,CHO_2	54·4	·945	·919	Odour of peach-kernels; used for flavouring arrack and rum.
" acetate, . .	$C_2H_5,C_2H_3O_2$	74·3	...	·908	Fragrant odour; solvent of morphia; see par. 296.
" butyrate, .	$C_2H_5,C_4H_7O_2$	120·	·902	...	Odour of pine-apples; used in fruit-essences. "Rum-essence" is obtained by distilling saponified butter with sulphuric acid and alcohol.
" valerate, .	$C_2H_5,C_5H_9O_2$	134·	...	·866	Odour of valerian.
" pelargonate,	$C_2H_5,C_9H_{17}O_2$	228·	...	·863	Odour of French brandy; used for flavouring factitious wines.
" benzoate, .	$C_2H_5,C_7H_5O_2$	213·	...	1·051	Fragrant odour.
" nitrite. . .	C_2H_5,NO_2	18·	...	·947	Odour of apples; used in medicine: see par. 316 *et seq.*
" nitrate, . .	C_2H_5,NO_3	86·3	1·132	...	Sweet; hot vapour is explosive.
" chloride, . .	C_2H_5,Cl	12·5	·921	...	Burns with smoky green-edged flame, producing HCl.
" bromide, .	C_2H_5,Br	40·7	1·473	1·419	Burns with difficulty, giving fine green flame without smoke, and giving off bromine.
" iodide, .	C_2H_5,I	71·6	1·975	1·931	Turns brown in the light, liberating iodine. Organic research, and aniline dyes.
Amyl acetate, . .	$C_5H_{11},C_2H_3O_2$	137·	·884	·876	Odour of jargonelle pears; see par. 317.
" butyrate, .	$C_5H_{11},C_4H_7O_2$	176·	...	·852	Fragrant odour.
" valerate, .	$C_5H_{11},C_5H_9O_2$	188·	...	·864	Odour of apples; used as a fruit-essence.
" nitrite, . .	C_5H_{11},NO_2	99·	·902	·877	Used in medicine; see par. 349.
" chloride, .	C_5H_{11},Cl	101·	·886	·874	Burns with luminous green flame producing HCl.
" iodide, . .	C_5H_{11},I	147·	1·468	...	Faint odour; turns brown in light.

From the above table it will be seen that the ethers of *monatomic* alcohol radicles form a very extensive and interesting series of bodies, some of them, as the nitrites of ethyl and amyl, and the acetate of ethyl, being employed in medicine, some in perfumery, others in the manufacture of coal-tar dyes, and many others are used for compounding artificial fruit-essences. The more important, and such as sometimes require chemical examination, are described in detail in separate paragraphs (296 *et seq.*). They may generally be assayed and analysed by methods similar to those employed for examining ethyl acetate. Sperm oil, spermaceti, and the *waxes* have also the constitution of ethers of monatomic alcohol radicles, but will be more conveniently considered in the division on "Fixed Oils and Fats."

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[1] In addition to the above, the salts of ethyl-sulphuric and ethyl-disulphocarbonic acids are employed, and are described in separate sub-sections in par. 304 *et seq.*

The ethers of *diatomic* alcohol radicles have received few practical applications, and do not require special description.

The ordinary natural fixed oils and fats may be regarded as ethers, of the *triatomic* alcohol-radicle containing glycyl, C_3H_5'''. By treatment with alkalies or high-pressure steam they yield glycyl alcohol (glycerin) and stearic, oleic, or other "fatty acid."

The detailed consideration of the fixed oils and fats may be conveniently deferred, as they form a true natural group, and do not present close physical analogies to the salts of monatomic alcohols, to which the term "ether" was originally, and with greater propriety, applied.

291. A general process for the analysis of compound ethers is based on their reaction with alcoholic potash or soda, which decomposes them with production of alcohol and formation of a salt of the alkali-metal, as in the following example :—

$$\underset{\text{Ethyl butyrate.}}{(C_2H_5)C_4H_7O_2} + \underset{\text{Potassium hydrate.}}{KHO} = \underset{\text{Potassium butyrate.}}{KC_4H_7O_2} + \underset{\text{Ethyl alcohol.}}{(C_2H_5)HO} .$$

The following are the details of the process, which is practically identical with that of Koettstorfer for the examination of fats :—

A volume of 50 c.c. (measured with the greatest attainable accuracy) of a solution containing about 60 grammes of caustic potash in 1 litre of pure rectified spirit is introduced into a strong bottle holding about 100 c.c.[1] A quantity of the ether, weighing from 4 to 6 grammes, is then added in such a manner as to avoid loss. The ether may be contained in a small glass bulb, or a known weight of the ether dissolved in pure alcohol may be added. The bottle is then closed with an india-rubber stopper which is to be firmly secured by wire, and is next exposed to a temperature of about 100° C. for half an hour, after which it is allowed to cool, opened, a few drops of phenol-phthaleïn solution added, and the liquid at once titrated with standard sulphuric or hydrochloric acid. A blank experiment is then made by heating 50 c.c. of the alcoholic potash alone for half an hour, and titrating with acid as before. The *difference* between the measure of standard acid required in the blank experiment, and that in which the ether was present, gives the measure of acid corresponding to the alkali neutralised by the ether. Each cubic centimetre of normal acid thus employed represents 0·0561 gramme of KHO, or, in other words, each 1 c.c. of *difference* between the measure of the acid originally employed, and that used in the blank experiment represents *one equivalent in milligrammes* of the ether present.[1]

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[1] The spirit should be previously distilled with addition of caustic potash.

The foregoing method of decomposing ethers with alcoholic alkaline solutions often furnishes valuable evidence of the purity of the substances examined. Thus an elementary combustion would scarcely detect 10 per cent. of ethyl alcohol in ethyl acetate, or of amyl alcohol in amyl acetate, but the above process would indicate the impurity with certainty.

292. After decomposing the compound ether with alkali as above described, and titrating the products with standard acid, a further knowledge of the ether may be obtained in the following manner:—The free alcohol is got rid of by distilling or evaporating the slightly alkaline liquid. The residue is treated with an amount of sulphuric acid fully sufficient to doubly neutralise the alkali originally added (*i.e.*, to effect the reaction $KHO + H_2SO_4 =$

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[1] As an example:—Suppose that 45 c.c. of normal acid were employed in the blank experiment, and that 8 c.c. were required after saponification of the ether. The difference of 37 c.c. represents the measure of normal alkali employed for the decomposition of the ether. As each centimetre of this contains 56·1 m. grms., or one equivalent in milligrammes, of KHO, it follows that the weight of ether employed contained a number of milligrammes equal to 37 times its equivalent. Supposing the weight of ether employed was 4·810 grammes, then its equivalent would be $\frac{4810}{37} = 130$. Of course, the equivalent thus found is identical with the molecular weight, one-half of the molecular weight, or one-third of the molecular weight, according to the constitution of the ether.

Conversely, if the equivalent of the ether were known to be 130, the weight of it present in the quantity of the sample taken would be $130 \times 37 = 4810$ milligrammes.

$KHSO_4 + H_2O$), and the liquid is distilled. The acid of the ether will be liberated, and, if volatile without decomposition, will pass more or less perfectly into the distillate, where it may be further examined, converted into a barium salt, &c.[1]

293. The foregoing method may be conveniently employed for the determination of chloroform and chloral hydrate when in alcoholic solution, the reactions being:—

a. With chloroform: $4KHO + CHCl_3 = KCHO_2 + 3KCl + H_2O$.
b. With chloral hydrate: $5KHO + C_2HCl_3O,H_2O = 2KCHO_2 + 3KCl + 2H_2O$.

The first reaction requires 4 equivalents, and the latter 5, of alkali. Hence, each c.c. of *difference* in the amounts of normal sulphuric acid required will represent 29·9 milligrammes of chloroform or 33·1 of chloral hydrate.

294. A. Dupré has applied the above process to the determination of the fixed and volatile ethers of wine. 250 c.c. of the wine are distilled down to about 50, and the distillate made up to 250 c.c. In 100 c.c. of this, the free volatile acid is determined by standard alkali, and another 100 c.c. is digested with a known excess of decinormal alcoholic soda. The extent to which this is neutralised over and above that due to the free acid represents the volatile ethers, which are best expressed in terms of acetic ether. To determine the fixed ethers (assumed to be ethyl tartrate), 250 c.c. measure of the wine is evaporated on a water-bath to about 40 c.c.[2] The residue is distilled with excess of caustic alkali, a little tannin being added to prevent frothing. The distillate contains the alcohol produced by the decomposition of the tartaric ether. It is rendered slightly acid with sulphuric acid, and again distilled, 20 c.c. being driven over. The alcohol in these 20 c.c. may be determined by the density, or preferably by the oxidation-method described in par. 161.

295. A useful general method of examining compound ethers was devised by Chapman and Smith (*Jour. Chem. Soc.*, xix. 477). It is based on the fact that organic bodies when oxidised in a sealed tube by a mixture of sulphuric acid and acid chromate of potassium, yield proximate products of oxidation closely related

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[1] It must be remembered, however, that if hydrochloric acid were used in the original titration more or less of it will appear in the distillate, unless excess of silver sulphate be added to the contents of the retort before distillation. Standard sulphuric may be substituted for the hydrochloric acid.

[2] With wine containing much sugar the residual liquid should be diluted, and the evaporation repeated.

to the radicles contained in them. Special applications of this process are given in pars. 137, 151, 161, 273, &c.

Shortly, the process consists in heating a known weight of the substance in a sealed tube for some hours with an aqueous solution of bichromate of potassium, containing from 3 to 8 per cent. of the salt, and 5 parts by weight of concentrated sulphuric acid to every 4 of the bichromate. The following reactions were verified by the authors of the method as occurring with very considerable accuracy :—

Ethyl alcohol,	$C_2H_6O + O_2$	$= HC_2H_3O_2 + H_2O.$
Amyl alcohol,	$C_5H_{12}O + O_2$	$= HC_5H_9O_2 + H_2O.$
Ethyl acetate,	$C_2H_5,C_2H_3O_2 + O_2$	$= 2HC_2H_3O_2.$
Amyl acetate,	$C_5H_{11},C_2H_3O_2 + O_2$	$= HC_2H_3O_2 + HC_5H_9O_2.$
Amyl valerate,	$C_5H_{11},C_5H_9O_2 + O_2$	$= 2HC_5H_9O_2.$
Amyl nitrite,	$C_5H_{11},NO_2 + O_3$	$= HC_5H_9O_2 + HNO_3.$
Ethyl nitrate,	$C_2H_5,NO_3 + O_2$	$= HC_2H_3O_2 + HNO_3.$
Ethyl iodide,	$2C_2H_5I + O_5$	$= 2HC_2H_3O_2 + H_2O + I_2.$
Isopropyl iodide,	$2CH_2(C_2H_5)I + O_{11}$	$= 2HC_2H_3O_2 + 2CO_2 + 3H_2O + I_2.$
Ethyl-amine,	$C_2H_5,H_2N + O_2$	$= HC_2H_3O_2 + NH_3.$
Ethyl-amyl-amine,	$C_2H_5,C_5H_{11},HN + O_4$	$= HC_2H_3O_2 + HC_5H_9O_2 + NH_3.$
Ethyl benzoate,	$C_2H_5,C_7H_5O_2 + O_2$	$= HC_2H_3O_2 + HC_7H_5O_2.$

Compounds containing methyl yield formic acid by oxidation, but the greater part of this is further oxidised to carbonic acid and water. Messrs Chapman and Smith (*Jour. Chem. Soc.*, xx. 173) further showed that the process was capable of being used for investigating the structure of isomeric bodies. This is exemplified in the equation representing the oxidation of isopropyl iodide.

The foregoing methods of examining ethers are of such general application, that, with the aid of the table on page 129, most of the ethers in common use may be readily identified, and even quantitatively determined. The assay of commercial ethers may usually be conducted as described in the following section on "Ethyl Acetate." A few, however, owing to their special properties or great individual importance, will be considered in separate sections.

296. **Ethyl Acetate.** Acetic Ether.

French—Ether acétique. *German*—Essigäther.

$$C_4H_8O_2 = C_2H_5,C_2H_3O_2 = \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\} O = C\left\{\begin{matrix}H\\ H\\ H\\ CO.O(C_2H_5).\end{matrix}\right.$$

Acetate of ethyl is best prepared by distilling dried sodium acetate with alcohol and sulphuric acid[1];—$(C_2H_5)HO + NaC_2H_3O_2 + H_2SO_4 = NaHSO_4 + (C_2H_5)C_2H_3O_2 + H_2O$.

The product of the distillation is best purified from alcohol by agitation with a saturated solution of calcium chloride, and subsequently dehydrated by contact for some days at the ordinary temperature with recently ignited potassium carbonate, or distillation over dried acetate of sodium. (The use of solid calcium chloride for dehydration causes considerable loss from the formation of a compound with the ethyl acetate, decomposed on addition of water.)

297. Ethyl acetate occurs in many wines and in wine-vinegar. It is produced spontaneously in several pharmaceutical preparations, notably in the tincture of ferric acetate. It possesses considerable solvent powers, and is especially employed for extracting morphine and tannins for aqueous liquids.

298. Pure ethyl acetate is a colourless liquid, of very fragrant, agreeable odour. When pure it has a density of about 0·908 at 15° C., and boils at 73·5 to 74·3° C. Ethyl acetate is miscible in all proportions with alcohol, ether, and chloroform, but is only sparingly soluble in water, requiring 8 measures at 0°, or 9 at 15° C. for its solution. The solubility of water in acetic ether is 1 measure in 26 at 0°, and 1 in 24 at 15° C. In a saturated solution of calcium chloride, ethyl acetate is but very slightly soluble, requiring 47 measures at 15° C. and almost as large a proportion at 0°.

299. COMMERCIAL ACETIC ETHER is often impure. In a series of eight samples representing the products of most of the leading makers, W. Inglis Clark found proportions of real ethyl acetate ranging from 90·14 to 30·6 per cent.; the alcohol from 7·2 to 48·0 per cent; the free acetic acid from a *trace* up to 7·0 per cent.; while the "water, ether, &c." (estimated by difference) ranged from 1·5 to 29·6 per cent.

300. For the analysis of commercial acetic ether, the following process gives satisfactory results :—

Dissolve 5 c.c. in proof spirit,[2] add a few drops of phenolphthaleïn, and titrate the *free acetic acid* by decinormal caustic soda. Each 1 c.c. of decinormal soda neutralised represents 0·006 gramme of $C_2H_4O_2$ in the 5 c.c. of sample used.

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[1] The best method of operating has been fully detailed in a paper by W. Inglis Clark (*Pharm. Jour.*, [3] xiii. 777), who has also placed on record much other valuable information on acetic ether.

[2] The spirit should be first freed from traces of free acid by adding a few drops of phenol-phthaleïn, and then dropping in dilute alkali till a faint pink tint remains after shaking.

Add to another quantity of 5 c.c. of the sample the same measure of decinormal soda which has been employed in the titration, and then saponify the neutralised liquid by alcoholic potash as described in par. 291. Each 1 c.c. of normal alkali neutralised by the sample represents 0·088 gramme of *ethyl acetate* in the quantity of the sample used; or 0·046 of alcohol regenerated from the ether.

Treat 20 c.c. of the sample with 20 c.c. of water and about 12 grammes of solid caustic potash in a flask furnished with an inverted condenser. After digesting for some time at the ordinary temperature, heat the flask to 100° C. for about two hours, add 20 c.c. of water, and distil over exactly 50 c.c. Ascertain the alcohol in the distillate by calculation from its density, divide the weight so found by 4, and subtract from the dividend the amount of alcohol derived from the saponification of the ether, as ascertained in the manner already described. The difference is the actual *alcohol* present in 5 c.c. of the sample.

By subtracting the sum of the *acetic acid*, *ethyl acetate*, and *alcohol* found as above from the weight of 5 c.c. of the sample, the amount of "*water, ether, &c.*" may be ascertained.

301. A very simple and approximately accurate method of ascertaining the proportion of real ethyl acetate present in commercial acetic ether consists in agitating 10 c.c. of the sample, in a graduated tube, with an equal measure of a saturated solution of chloride of calcium. The volume of the layer which rises to the surface is the quantity of ethyl acetate in the measure of the sample examined. The results are fairly accurate, if the water and alcohol of the sample do not together much exceed 20 per cent. by measure, but with larger proportions the volume of ether which separates is sometimes notably below the real amount of ethyl acetate present. The error may be avoided in some measure by adding to the sample twice its measure of acetic ether which has been previously treated with calcium chloride solution. 20 c.c. of the fortified sample should then be shaken with 20 c.c. of calcium chloride, when the diminution in the volume of the ethereal layer will represent the measure of impurities in $\frac{20}{3}=6·67$ c.c. of the sample.

The foregoing method of operating is due to W. Inglis Clark. The employment of water previously saturated with washed acetic ether, and coloured with fuchsine (see par. 323) does not give satisfactory results. (Both the German and the United States Pharmacopœias require that when acetic ether is shaken up with an equal volume of water, the water shall not be augmented more than $\frac{1}{10}$ of its original volume.)

302. The specific gravity of ethyl acetate is not a satisfactory indication of its purity, as it dissolves alcohol, ether, and chloroform in all proportions, and may be diluted with spirit of approximately the same density as the pure substance.

303. Acetic ether should not contain more than a trace of free acid, and should be entirely volatile without residue.

304. Ethyl-Sulphates. $M',C_2H_5SO_4 = \left.\begin{matrix} C_2H_5 \\ M' \end{matrix}\right\} SO_4$.

The ethyl-sulphates or "sulphovinates" are the salts of ethylsulphuric acid, which body has the composition of an ethylhydrogen sulphate, but possesses decided acid properties, and forms a well-defined series of salts. Hence it might with equal propriety be considered among the *acid* derivatives of the alcohols.

305. Ethyl-sulphuric acid is produced by the reaction of alcohol on strong sulphuric acid, thus :—$C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O$. The change is much facilitated by keeping the liquid at a temperature of 100° C. for 24 hours. The less water there is present, the more perfect the change ; but the reaction is always far from complete. If the temperature be raised much above 100° C., ordinary ether is produced, and, at higher temperatures still, ethylene and other products are formed.

306. From the crude ethyl-sulphuric acid, obtained as above, *barium ethyl-sulphate* may be prepared by neutralising the product with carbonate of barium, filtering off the insoluble barium sulphate, and evaporating the filtrate to crystallisation. The *calcium* salt may be obtained in similar manner, and the *lead* salt by employing litharge instead of barium carbonate.

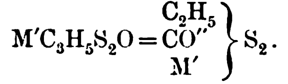
307. Sodium ethyl-sulphate, $NaC_2H_5SO_4 + H_2O$, may be obtained by decomposing one of the above salts with sodium carbonate, or by adding powdered carbonate of sodium and alcohol, or alcoholic solution of caustic soda, to the crude acid, filtering from the insoluble sodium sulphate, and evaporating the filtrate to crystallisation.

Sodium ethyl-sulphate (sulphovinate of sodium), is a white crystalline salt of faint ethereal odour, and cooling, sweetish, somewhat aromatic taste, very deliquescent, soluble in 0·7 parts of cold water, and also soluble in alcohol, with which it is capable of forming a crystalline compound. Sodium ethyl-sulphate is insoluble in ether. It has been employed in medicine as a saline purgative. At 86° C. sodium ethyl-sulphate melts and becomes anhydrous; at 120° C. it decomposes, evolving alcohol vapour, and leaving acid sulphate of sodium. It also decomposes spontaneously at ordinary temperatures, especially when in solution, with formation of sodium sulphate. The presence of a little free alkali prevents this change. The commercial salt is liable to contain barium, calcium, lead, arsenic, sulphates, &c. It is not unfrequently contaminated with foreign organic matter. When pure it does not char on ignition. It has been adulterated by admixture with sulphate of sodium, and has been replaced by acetate of barium. The last dangerous substitution would at once be detected by adding dilute sulphuric acid to the aqueous solution.

308. The characters of the ethyl-sulphates are sufficiently indicated by the above description of the sodium salt. They are soluble in water. When heated with dilute sulphuric acid they evolve alcohol, and with strong sulphuric acid, ether. With sulphuric acid and an acetate they give a fragrant odour of acetic ether. The same result is obtained by simply heating together an acetate and sulphovinate.

309. Ethyl-Sulphuric Acid, $HC_2H_5SO_4$, may be obtained in a state of purity by decomposing the barium salt by an equivalent amount of dilute sulphuric acid, or a solution of ethyl-sulphate of lead by sulphuretted hydrogen. On concentrating the filtered liquid, sulphovinic acid is obtained as a limpid, oily, very sour, unstable liquid of 1·31 sp. gr. It is miscible with water and alcohol in all proportions, but it is insoluble in ether.

310. Ethyl Disulpho-Carbonates; Xanthates.



$$M'C_3H_5S_2O = \left.\begin{matrix} C_2H_5 \\ CO'' \\ M' \end{matrix}\right\} S_2.$$

The xanthates are the salts of xanthic acid, which, though having the composition of an ether, possesses decided acid properties. Hence, it ought strictly to be considered among the *acid* derivatives of the alcohols.

311. When boiling absolute alcohol is saturated with pure caustic potash, and carbon disulphide added gradually till it ceases to be dissolved, or the liquid becomes neutral, potassium xanthate is formed according to the equation:—$C_2H_5HO + KHO + CS_2 = KC_2H_5COS_2 + H_2O$.

On cooling, the xanthate of potassium crystallises in slender colourless prisms, which must be pressed between blotting paper and dried in a vacuum. Potassium xanthate is readily soluble in water and alcohol, but insoluble in ether. On exposure to air it suffers gradual decomposition.

312. On adding dilute sulphuric or hydrochloric acid to potassium xanthate, xanthic acid, $HC_3H_5S_2O$, is liberated as a colourless, heavy, oily liquid, of peculiar and powerful odour and astringent bitter taste. It is very combustible. Xanthic acid

reddens litmus, and ultimately bleaches it. At a very slight rise of temperature it undergoes decomposition into alcohol and carbon disulphide. Owing to this property the xanthates have been successfully used as a remedy for the *phylloxera*, which attacks the vine, and is equally efficacious against the ravages of other noxious insects. The xanthate is mixed with earth, either alone or together with superphosphate, when it gradually undergoes decomposition with formation of carbon disulphide.

Xanthic acid possesses powerful antiseptic properties.

Xanthate of sodium is employed to effect the reduction of ortho-nitrophenylpropiolic acid to indigo-blue.

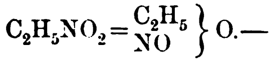
When warmed with nitric acid, xanthic acid and xanthates evolve an odour of ethyl nitrite.

On distillation, the xanthates are decomposed with formation of CO_2,CS_2,H_2S, and a peculiar sulphuretted oil, while a metallic sulphide and carbon remain behind.

313. The most characteristic reaction of xanthic acid, and the one from which it derived its name, is that produced with salts of copper. On adding cupric sulphate to a neutral solution of a xanthate a brownish precipitate of cupric xanthate is first formed, which quickly changes to bright yellow flocks of cuprous xanthate. This substance is insoluble in water and in dilute acids, but is decomposed by strong acids. It is slightly soluble in alcohol, and rather more so in carbon disulphide, and is said to be insoluble in ammonia. It is not sensibly attacked by sulphuretted hydrogen, but is instantly decomposed by a soluble sulphide. The formation of cuprous xanthate has been employed for detecting carbon disulphide in coal-gas, the gas being passed through alcoholic potash, the excess of alkali neutralised by carbonic or tartaric acid, the insoluble salt removed by filtration, and the liquid treated with sulphate of copper.

314. The formation of cuprous xanthate has also been proposed by E. A. Grete (*Jour. Chem. Soc.*, xxx. 551) as a means of determining copper and caustic alkali, and has been applied by B. Nickels to the determination of carbon disulphide in commercial benzols. The method of the latter chemist is essentially an estimation of xanthate by a standard solution of copper.

315. Xanthates may also be estimated by titration with a standard solution of iodine (C. Vincent, *Ann. Chem. Phys.*, [5] xxii. 544), or by oxidation with permanganate, and precipitation of the resultant sulphate by barium chloride (H. L. Greville, *Jour. Soc. Chem. Ind.*, ii. 490).

316. **Ethyl Nitrite.** Nitrous ether. 

$C_2H_5NO_2 = \left.\begin{matrix} C_2H_5 \\ NO \end{matrix}\right\} O.$—

This substance has been known in an impure state for a long time. It may be obtained by passing the red vapours of nitrogen trioxide (evolved by acting on starch by nitric acid) into alcohol; by distilling nitrite of potassium or sodium with alcohol and sulphuric acid; or by the direct action of nitric acid on alcohol. In the last case the nitric acid is reduced by a portion of the alcohol, and the nitrous acid so formed acts on the remainder to form ethyl nitrite. A considerable quantity of aldehyde results from the oxidation of the alcohol, so that the ether obtained by this process is largely contaminated. This reaction may be avoided in great measure by adding metallic copper to the contents of the retort.

317. Pure nitrite of ethyl is a nearly colourless liquid, of very fragrant odour. It is soluble in all proportions in alcohol, but requires forty-eight parts of water for solution. It boils at 18° C., and has a density of ·947 at 15·5° C. (60° F.). It is liable to decompose on keeping, especially in presence of water. It gives many of the ordinary reactions of the nitrites. Thus, when mixed with a little dilute sulphuric acid, and poured on a strong aqueous solution of ferrous sulphate, it develops a dark brown colour; when dissolved in alcohol, and treated with a few drops of dilute sulphuric or acetic acid, it liberates iodine from potassium iodide, and therefore the mixture produces the well-known blue colour on addition of starch.

318. Spirit of Nitrous Ether.

French.—Ether azoteux alcoolisé. *German.*—Versüsster salpetergeist.

"Spirit of Nitrous Ether[1]" (*spiritus ætheris nitrosi*, B.P.) is the present official name of a preparation consisting essentially of a solution of impure ethyl nitrite in rectified spirit. Spirit of nitrous ether is the modern representative of the old "Sweet

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[1] The literature of spirit of nitrous ether is somewhat extensive. The following is a list of references to it in comparatively recent volumes of the *Pharmaceutical Journal*:—

B. H. Paul, [3] vii. 1071.
F. W. Rimmington, [3] viii. 341, 362, 377; x. 41, 220.
J. Williams, [3] viii. 441, 453.
W. Smeeton, [3] x. 21.
A. Dupré, [3] x. 93.
J. Muter, [3] x. 94.
W. Pollard, [3] x. 100.
J. F. Eykman, [3] xiii. 63.
W. H. Symons, [3] xiv. 281.
U.S. and German Preparations, [3] xiv. 101.
D. J. Leech, [3] xiv. 322.
A. C. Abraham, [3] xiv. 390, 876, 915.
P. MacEwan, [3] xiv. 817, 826, 896, 936.
D. B. Dott, [3] xiv. 819, 826, 895; xv., 200, 492, 592.
T. S. Dymond, [3] xv. 101.

Spirit of Nitre" (*Spiritus nitri dulcis*, P.L. 1745) which was prepared by distilling together rectified spirit and nitric acid. In the London Pharmacopœia of 1787, it is called *Spiritus Ætheris nitrosi*, which name was modified in the London Pharmacopœia of 1809 to *Spiritus Ætheris nitrici*. The essential nature of the product was clearly recognised in 1809, a translation of the London Pharmacopœia of that date containing a note referring to the brown coloration with ferrous sulphate, and to the difficulty attending the separate preparation of "nitric ether." The name "spirit of nitric ether" was retained in subsequent London Pharmacopœias, including the last, published in 1851. The nearly contemporary Dublin Pharmacopœia described it as *spiritus ætherеus nitrosus*, and directed that it should be made by dissolving previously prepared ethyl nitrite in rectified spirit. While the name of the preparation of the London Pharmacopœia of 1851 clearly indicated the intention that the product should contain ethyl nitrite or nitrate as an essential constituent, the process of manufacture prescribed led in practice to the production of an article of exceedingly variable character. The reaction was of a very complex nature, and, even in experienced hands, the product sometimes contained only a comparatively small proportion of nitrous ether, while the amount of aldehyde formed by the oxidation of the alcohol was considerable. In the British Pharmacopœia of 1867, the name of the preparation was changed to "spirit of nitrous ether." The method of preparation was also modified, an addition of metallic copper being directed to be made to the contents of the retort, whereby the nitric acid is largely converted into nitrous acid, which then acts on the alcohol with formation of ethyl nitrite. The use of copper prevents, in great measure, the formation of aldehyde, and gives a distillate richer in nitrous ether than that obtained by the old process.[1]

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[1] A large majority of respectable Pharmacists, when asked for "sweet spirit of nitre," recognise the "spirit of nitrous ether, B.P." as the modern and official representative of that preparation, and supply their customers with it accordingly. Some firms still manufacture an article of the nature of the "spirit of nitric ether, L.P.," and sell it under the name of "sweet spirit of nitre," and an article of a density of ·900 appears on the price-lists of certain wholesale houses. Such a practice is highly objectionable, as a preparation of such a density will either be destitute of nitrous ether when made, or will very shortly become so. Sweet spirit of nitre prepared by the process of the London Pharmacopœia of 1851 has a pleasanter taste than the B.P. article, which may account for the alleged preference of the public for the former. It is, however, asserted that many medical practitioners prefer the L.P. preparation, which, if true, is not improbably due to their being asked whether they wish to be served with "the 845 or the 850 article," and erroneously

319. The characters of "spirit of nitrous ether" are thus described in the British Pharmacopœia of 1867 :—"Transparent and nearly colourless, with a very slight tinge of yellow, mobile, inflammable, of a peculiar penetrating apple-like odour, and sweetish, cooling, sharp taste. Specific gravity, 0·845. It effervesces feebly, or not at all, when shaken with a little bicarbonate of soda. When agitated with solution of sulphate of iron and a few drops of sulphuric acid, it becomes a deep olive-brown or black. If it be agitated with twice its volume of saturated solution of chloride of calcium in a closed tube, 2 per cent. of its original volume will separate in the form of nitrous ether, and rise to the surface of the mixture." In later reprints of the British Pharmacopœia of 1867, the words "an ethereal layer" are substituted for "nitrous ether" in the last sentence.

320. The spirit of nitrous ether of the German Pharmacopœia has a density of 0·840 to 0·850, while the U.S. preparation has a density of 0·823 to 0·825, and is described as containing between 4 and 5 per cent. of ethyl nitrite (see par 339).

321. Spirit of nitrous ether is a liquid of very complex composition. Besides the ethyl nitrite, alcohol, and water which may be regarded as its normal constituents, it usually contains aldehyde, and probably paraldehyde and ethyl acetate and nitrate. After keeping, sensible quantities of free nitrous and acetic acids are developed, and other changes occur. In addition to the foregoing constituents, the occurrence of which is generally admitted, according to Eykman (*Pharm. Jour.*, [3] xiii. 63) spirit of nitrous ether is also liable to contain ethyl oxide (ether); ethyl formate and oxalate; cyanogen compounds; glyoxal; glyoxalic, oxalic, malic, and saccharic acids; &c.[1]

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assuming that the higher figure indicates a greater strength (combined with the advantage of a lower price).

In Cooley's *Cyclopædia of Practical Receipts* (sixth edition, 1880, page 1545) it is stated that much of the spirit used for making sweet spirit of nitre of ·850 specific gravity is a waste product from the manufacture of fulminating mercury, and as such frequently contains no inconsiderable quantity of hydrocyanic acid.

[1] To this formidable list, the author suggests the addition, as a possible constituent, of *nitro-ethane* ($C_2H_5NO_2 = CH_3.H_2C.NO_2$), a body isomeric with ethyl nitrite, but having a density of 1·058 and boiling at 111° to 113° C.

Although the ethyl nitrite is the most characteristic constituent of spirit of nitrous ether, and all the processes of preparation and tests of quality aim at obtaining a product containing it in quantity, it is supposed by some that the nitrite of ethyl is not the only constituent of value in spirit of nitrous ether. There appears to be little foundation for this view. There are even those who contend that nitrous ether is not an essential constituent of the I.P. prepara-

322. The composition of spirit of nitrous ether varies very considerably, and but few analyses have been made showing the proportions even of the principal components (other than ethyl nitrite), and in these cases the determinations have not been made by unexceptionable methods. The following analyses by F. M. Rimmington [1] are the most complete hitherto published:—

	Ethyl Nitrite.	Nitrous Acid.	Acetic Acid.	Aldehyde.	Alcohol.	Water.
1. Agreeing with B.P. tests,	1·69	0·59	0·47	1·19	88·10	7·96
2. ,, ,, .	1·72	0·56	0·50	1·19	88·10	7·93
3. Commercial "Best," .	0·75	0·29	0·16	0·75	87·50	10·55
4. ,, ,, .	0·17	0·27	0·03	0·21	85·20	14·12
5. ,, ,, .	0·10	0·69	0·18	0·26	82·60	16·17
6. ,, ,, .	0·07	0·68	0·16	0·00	83·60	15·49

The following analyses are by P. MacEwan.[2] Being all made by the same method, they are interesting as showing the increase in the proportion of aldehyde and free acids by keeping, but some of the figures have probably more a relative than an absolute value:—

	Ethyl Nitrite.	Nitrous Acid.	Acetic Acid.	Aldehyde.
1. B.P. Spirit, old sample,.	0·87	0·47	1·20	0·80
2. B.P. One week old, .	3·54	0·22	0·21	0·85
Two weeks old, .	...	0·26	0·25	0·95
Three weeks old, .	3·14	0·27	0·35	...
3. B.P. Two days old, .	2·01	...	...	0·80
Four days old, .	...	0·24	0·22	1·14
Seven days old, .	1·24	0·32	0·25	2·00
4. B.P. One month old, .	1·93	0·24	0·41	1·67
5. L.P. Spirit, four months old,	3·53	0·16	0·29	1·50
6. ,, ,, ,, .	1·64	0·35	0·49	1·43
7. ,, ,, . .	0·22	0·19	0·25	0·20

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tion, on the ground that it may be so made as to be nearly destitute of nitrous or nitric compounds. Such a product appears to bear the same relation to a well-made preparation that diseased milk does to the milk from a healthy cow.

[1] *Pharm. Jour.*, [3] x. 41. In these analyses the ethyl nitrite is probably considerably understated, at least in the case of the first two samples. In making the analysis, the *nitrites* were reduced by a copper-zinc couple, and the resultant ammonia distilled off and titrated with standard acid. The *free acids* were determined by evaporating 10 c.c. with potassium carbonate, and separating the acetate and nitrite in the residue by means of alcohol (making an allowance of 0·021 gramme for KNO_2 dissolved in 10 c.c. of alcohol). The *aldehyde* was determined by treating the sample with 10 c.c. of hydrogen peroxide, and noting the increase in the acidity. The *alcohol* was deduced from the density of the sample, and the *water* estimated by difference.

[2] *Pharm. Jour.*, [3] xiv. 817. In these analyses, Eykman's method (measure-

323. The tendency of spirit of nitrous ether and kindred preparations to undergo gradual deterioration with destruction of the nitrous ether is a point of great practical importance. The exact conditions which facilitate or retard the change are not thoroughly understood, but it is established beyond doubt that the presence of excess of water greatly favours the destruction of the nitrous ether. Hence adulteration of sweet spirit of nitre, &c., with water, a practice which is very common, not only dilutes the preparation, but greatly enhances the tendency of the nitrous ether to undergo decomposition. The author proved, by direct experiment, that a sample of spirit of nitrous ether kept perfectly well for very many months when undiluted, but the same sample when mixed with one-third of its measure of water contained no nitrous ether whatever after an interval of four months. In these experiments the samples were kept in well-closed bottles, but of course imperfect closing of the bottle, or exposure to light or to excessive temperature, will be certain to cause loss of so volatile a substance as is the nitrite of ethyl.[1] On the other hand, a solution of pure

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ment of nitric oxide, par. 331), was employed for estimating the ethyl nitrite. The free acids were ascertained by titrating in succession with methyl-orange and phenol-phthaleïn as indicators, and the aldehyde was estimated by Thresh's colorimetric method (par. 394).

[1] The presence of water, even in moderate proportion, greatly increasing the tendency to change, and the ordinary spirit of nitrous ether being of uncertain strength and composition, Mr John Williams has proposed to substitute for it a solution of pure ethyl nitrite in nine or nineteen times its weight of absolute alcohol. Such a preparation appears to be remarkably permanent, and if rectified spirit were substituted for the absolute alcohol the solution would still be very stable, but unfortunately these preparations are not found to have the flavour of ordinary spirit of nitrous ether, though the difference may have been largely due to greater concentration of the solution. Similarly, Mr Williams experimented with aldehyde, the flavour of which was highly objectionable, and with a mixture of aldehyde and ethyl nitrite dissolved in alcohol, and has recently suggested that sweet spirit of nitre may contain the polymer of aldehyde known as paraldehyde, which it closely resembles in flavour. Paraldehyde, however, is more sedative in effect than diuretic, like sweet spirit of nitre, so that the strong probability is that the therapeutic value of the preparation really lies in the ethyl nitrite, and possibly in the nitrous acid or other nitrous compounds which may be present. This view is strongly endorsed by Professor Matthew Hay, who writes—"With regard to the sweet spirit of nitre my opinion is that its most active ingredient ought to be the nitrite of ethyl. The nitrite is very active even in very small quantity, and I believe that if a preparation could be obtained containing a constant proportion of nitrite of ethyl, it would be a great gain to practical pharmacy and to therapeutists. The unreliability of the common forms of it has, I believe, led largely in recent years to its disuse. Murrell

nitrous ether in absolute alcohol was found by the author to contain a considerable proportion of ethyl nitrite, and mere traces of free acid, after being kept for fully seven years.

324. Analysis of Spirit of Nitrous Ether.

The assay of spirit of nitrous ether is somewhat difficult, on account of the complex character of the preparation.[1] Of the B.P. tests (par. 319) the density, behaviour with sodium bicarbonate, and reaction with ferrous sulphate in presence of free acid are

states that nitro-glycerine is powerfully diuretic, and I have shown that nitro glycerine is decomposed into nitrite in blood, hence its physiological action—hence diuresis." The subject has been further investigated by Dr D. J. Leech (*Practitioner*, October 1883), who writes to the author:—"I cannot agree with the contention of the drug trade that the medicinal value of the drug is not connected with the nitrous ether it contains." "After trying the effects of the various individual substances which spirit of nitrous ether contains, I can come to no other conclusion than that the nitrous ether is the chief, if not the only, active ingredient." "We have carefully analysed in our pharmaceutical laboratory (Owens College, Manchester), samples of spirit of nitrous ether prepared in various ways, and although we found traces of many other products, such as nitric ether, aldehyde, paraldehyde, &c., still of none of these is there sufficient to act medicinally."

Professor J. Attfield, again, has expressed his views in the following words (*Pharm. Jour.*, [3] viii. 454):—"He did not disparage the use of so ancient and excellent a medicine when properly prepared. At the same time it was well known that many medical men had considered that sweet spirit of nitre was altogether valueless. The reason was, doubtless, that some samples of the article sent into pharmacy for the use of medical practitioners had been little else than spirit of wine." "He himself was under the impression that the active principle of sweet spirit of nitre was the nitrite of ethyl, and he was led to that conclusion mainly by the researches of Dr Richardson, who had experimented largely upon the nitrites."

[1] The original edition of the British Pharmacopœia of 1867 stated that spirit of nitrous ether, on agitation with twice its measure of a saturated solution of calcium chloride, yielded "2 per cent. of its original volume in the form of nitrous ether," but Dr Redwood has since deprecated this statement (*Pharm. Jour.*, [3] viii. 377, 455), and, on his recommendation, the reprints of the British Pharmacopœia of 1867 state that 2 per cent. of "an ethereal layer" will rise, which according to Dr Redwood represents 10 per cent. of ether in the original liquid. But it has been found that the ethereal layer is by no means pure nitrite of ethyl, containing as it does a proportion of that body variously estimated, but admittedly not exceeding 50 per cent. Besides the uncertainty due to this cause, no ethereal layer whatever can be obtained from samples slightly poorer in ethyl nitrite than the newly made B.P. spirit, so that the test is worthless even as a rough means of assaying commercial spirit of nitrous ether. It may be applied to samples giving no indication in their original condition, by saturating 100 c.c. of the liquid with dry calcium chloride, distilling off 20 c.c. at a gentle heat, and treating the distillate with twice its measure of a saturated solution of calcium chloride.

serviceable; but the test with solution of calcium chloride is worthless and absolutely misleading.

The following methods are the most satisfactory of the many which have been devised for the examination of commercial spirit of nitrous ether:—

325. *Water* can be estimated with sufficient accuracy by taking the density of the sample. The B.P. spirit has a density of 0·845, but a slightly higher density may be tolerated. If, however, the specific gravity of the sample exceed 0·853, the presence of an excessive proportion of water may be considered proved. Commercial samples of sweet spirit of nitre are sometimes adulterated so largely with water as to bring the density to 0·910 or even higher,[1] an inferior spirit of 0·900 specific gravity being sold wholesale. A density of 0·845 corresponds, according to the alcohol tables in par. 156, to a content of 81·7 per cent. by weight of absolute alcohol, or 152·4 per cent. by volume of proof spirit. The extent to which a sample has been diluted with water may be found by multiplying the percentage of proof spirit (as found by the table) by the factor ·656 ($=\frac{100}{152 \cdot 4}$), when the product will be the percentage by volume of spirit of nitrous ether of B.P. density contained in the sample. To find the percentage by measure of spirit of ·850 density originally present, the percentage of proof spirit in the sample should be multiplied by ·673 ($=\frac{100}{148 \cdot 8}$).

The nitrous ether, though denser than alcohol, is present in too small a proportion to affect sensibly the estimation of water from the density. The addition of water to sweet spirit of nitre is a highly reprehensible practice, for it not only reduces the immediate strength and medicinal value of the preparation, but also renders it far more liable to change, owing to the tendency of ethyl nitrite to undergo decomposition in presence of water.

326. *Free Acid* will be indicated by the reaction with litmus paper, and by the effervescence occasioned on adding bicarbonate of sodium to the sample. The presence of notable proportions of free acid renders spirit of nitrous ether incompatible with potassium iodide, from which it liberates iodine.[2] The proportion of

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[1] The author recently examined a sample having a density of 0·940, which was very naturally devoid of nitrous ether.

[2] A sample of spirit of nitrous ether, which gave no perceptible effervescence with sodium bicarbonate, liberated a considerable amount of iodine from potassium iodide. After being agitated with sodium bicarbonate and left in contact with the salt for twenty-four hours, a notable quantity of iodine was still liberated and nitric oxide gas evolved; but when neutral sodium carbonate was employed instead of the acid carbonate, mere traces of iodine and gas were liberated on addition of potassium iodide.

acid may be ascertained by titration with standard alkali, but, as some samples of sweet spirit of nitre contain both free acetic and free nitrous acid, it is sometimes of interest to determine them separately, which is done by P. MacEwan in the following manner:—10 c.c. measure of the sample is placed in a flask in which a drop of phenol-phthaleïn solution has been previously put, and two or three drops of methyl-orange solution are next added. A porcelain slab, spotted with drops of methyl-orange solution, is arranged in readiness. A semi-normal solution of caustic soda (= 20 grammes NaHO per litre) is then rapidly added to the contents of the flask, and as soon as the red colour begins to fade, a drop of the liquid is removed by a glass rod and brought in contact with a spot of the methyl-orange on the plate. If the spot assume a pink tint, the nitrous acid is not quite neutralised, in which case the addition of the alkali solution is continued, until, on re-testing, a spot of methyl-orange is rendered only faintly pink. The volume of standard alkali used is then noted, and the titration continued until the pink tint produced by the phenol-phthaleïn denotes alkalinity. Each c.c. of semi-normal alkali first used represents 0·0235 gramme of nitrous acid (HNO_2), while each c.c. of the additional alkali requisite to produce the phenol-phthaleïn reaction corresponds to ·0300 gramme of acetic acid ($HC_2H_3O_2$). The process is approximate only.

327. *Aldehyde* will be indicated by the brown coloration produced on heating the sample with caustic potash. A sample free from an excessive proportion of aldehyde, when treated at the ordinary temperature with half its volume of a dilute solution of caustic potash, assumes a yellow colour, which gradually deepens but does not become brown in twelve hours.

For the determination of aldehyde, F. Rimmington treats the sample with hydrogen peroxide, and ascertains by titration the amount of (acetic) acid over that previously present. A preferable method is to treat 5 or 10 c.c. of the spirit by Thresh's colorimetric method, as described in par. 394.

The proportion of aldehyde present in preparations made by the old processes is much larger than in the "spirit of nitrous ether, B.P."

328. *Ethyl Chloride* and other *chlorinated bodies* may be detected by igniting a little of the sample in a porcelain basin, and holding a beaker moistened with nitrate of silver solution over the flame. If chloride of silver be formed, the sample may be evaporated with pure caustic soda and the chloride in the residue determined.

329. *Ethyl Nitrite* may be detected by the brown coloration produced by adding ferrous sulphate to an acidulated solution of the sample of spirit. Of various ways of making the test, the

author has found the following mode of operating to be the most delicate and reliable:—10 c.c. of the spirit is mixed with 5 c.c. of a strong aqueous solution of ferrous sulphate. Pure, concentrated sulphuric acid should next be poured down the side of the test-tube in such a manner as to form a distinct stratum under the spirituous mixture. A brown zone will thereupon be produced at the junction of the two layers, the intensity of which is an indication of the strength of the sample in nitrous ether. With good samples, the coloration is increased and extended by causing the layers to become partially mixed, but with inferior specimens the brown colour is more or less destroyed by such treatment.[1]

330. W. H. Symons proposes to obtain rough quantitative results by dissolving 1 part of ferrous sulphate in 5 of dilute sulphuric acid, and adding to 10 c.c. of this solution 1 c.c. of the sample to be tested. The coloration produced is compared with that yielded by a standard specimen or a solution of a nitrite.

331. The process of J. F. Eykman for assaying spirit of nitrous ether is practically a quantitative application of the iron reaction, but, instead of relying on the depth of the brown coloration, the nitric oxide gas evolved is collected and measured. Eykman's process has given excellent results in the hands of P. MacEwan and F. S. Dymond.[2] Their reports have been confirmed in the main by an extensive experience of its capabilities in the writer's own laboratory, where the accuracy of the process has been fully verified when a known quantity of pure sodium nitrite is employed. With solutions of ethyl nitrite several sources of error exist, which tend to cause the method to give results somewhat below the truth. The following is the mode of operating the author has found preferable, and it must be strictly followed to ensure results having the nearest approach to accuracy:—

To a small, round-bottomed, tubulated flask (A, fig. 9) is adapted a well-fitting rubber stopper, through which passes a narrow glass tube B, which extends nearly to the bottom of the flask, the end being drawn out to a point and turned up, so as to prevent any gas from entering.[3] Outside the flask the tube is bent over and connected by an india-rubber joint with a narrow vertical tube C, the lower end of which is drawn out to a point and arranged to reach nearly to the bottom of a conical glass D. The side-tube E of the flask is connected by a few inches of india-rubber F with the stopper of a Lunge's nitrometer G. The nitrometer is filled with solution of soda of about 1·10 specific gravity, which should be previously freed from dissolved oxygen by agitating it with a little ferrous sulphate, and allowing the precipitated oxide of iron to subside. A solution of ferrous sulphate is prepared by dissolving 100 grammes of the powdered crystallised salt in 500 c.c. of water, and adding 0·5 c.c. of strong sulphuric acid. A dilute sulphuric acid is prepared by diluting one volume of the strong acid (free from nitrous compounds) with three measures of water.

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[1] Some samples of spirit of nitrous ether give a brown coloration with the ferrous solution alone, a reaction which might be attributed to free nitrous acid. A sample which had been thoroughly agitated with neutral sodium carbonate gave no immediate reaction with ferrous sulphate solution, but in the course of a few minutes a strong brown colour was developed.

[2] D. B. Dott has confirmed the general accuracy of the process, and has found the results very constant, even when the conditions of the experiment are varied.

[3] The side-tube at the flask should be situated only just below the rubber-stopper, and not strictly as represented in the figure.

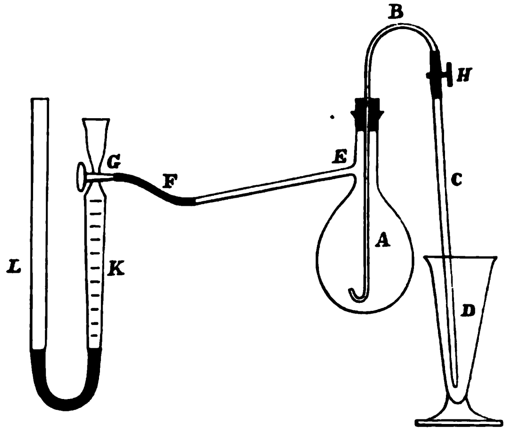

Fig. 9.

In commencing an experiment, about 30 c.c. of the iron solution should be poured into the flask, and the india-rubber cork well wetted and adjusted firmly in the neck. The flask is then connected with the nitrometer, the tap of the latter being closed and a small quantity of soda solution being contained in the cup. The tube C is immersed in the solution of iron contained in the glass D, and the screw-clip at H is open. The flask is then warmed to expel some of the air through C, when the source of heat is removed, and about 30 c.c. of iron solution is allowed to enter the flask, when the clip at E is firmly closed. The contents of the flask are then heated to boiling, and when the india-rubber at F shows signs of internal pressure, the tap G is opened, and the air from the flask allowed to bubble out through the soda contained in the cup of the nitrometer. When the air is thoroughly expelled the tap G is closed, the source of heat is removed, and the contents of the flask allowed to become quite cool. From 5 to 10 c.c. of the sample (according to its strength) is then placed in the conical glass, and diluted with 10 to 20 c.c. of water containing 1 or ·2 grammes of common salt. The clip F is then cautiously opened, and the vacuous liquid allowed to flow into the flask until the orifice of the tube C is only just covered. A little iron solution is then poured into the conical glass together with 5 c.c. of the dilute sulphuric acid, and this in its turn allowed to enter the flask. This is repeated until the liquid in the glass and tube is no longer coloured brown, care being taken not to allow any air to pass into the flask. The clip at H is then permanently closed and the contents of the flask heated to boiling. As soon as the india-rubber connection with the nitrometer shows signs of pressure, the tap G is turned so as to open communication between the flask and the graduated tube of the nitrometer K, when the nitric oxide gas produced by the reaction passes into K and is there collected. The process is stopped as soon as the contents of the flask are no longer brown, the tap G being closed and the clip at H simultaneously opened, when the liquid in the flask is forced back into A and the apparatus is in order for another experiment.[1] After standing half an hour to acquire the temperature of the air, the volume of gas in the nitrometer is observed, care being previously taken to adjust the level of the liquid in K with that in the open limb L. After reading off the volume of gas it is allowed to escape into the cup, when the nitrometer is ready to receive the gas evolved in another experiment.

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[1] Although the manipulation involved in the process is difficult to describe, it is very simple in practice, and when everything is ready the whole operation does not occupy more than fifteen minutes. Care must be taken to open and close the tap and clip at the right moment, and to avoid the introduction of any air by leakage or faulty manipulation. In the original apparatus employed by Eykman the gas is collected in a graduated tube arranged over a glass basin containing soda solution, but the use of a nitrometer furnished with a three-way tap is a decided improvement, in the opinion of the author, though many operators may prefer to adhere to the original arrangement. According to Eykman's original instructions the sample is to be mixed with the acid and ferrous sulphate solution before introducing it into the flask, but this procedure seems liable to occasion loss of gas from strong samples. If the liquid in the flask be not tolerably cool when the solution of the ether is allowed to enter, some of the ethyl nitrite may be volatilised undecomposed. The instruction to add some sodium chloride is not in accordance with the practice of Eykman, but it adds materially to the accuracy of the process, in the experience of the writer. It is important to conclude the operation as soon as the contents of the flask no longer have a brown colour, and the steam has driven the nitric oxide into the nitrometer-tube. In the case of strong samples the measure of reagents employed should be increased.

332. The following is the reaction occurring in the foregoing process :— $2C_2H_5NO_2 + 2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2C_2H_6O + 2NO$. Thus, 75 parts by weight of ethyl nitrite evolve 30 of nitric oxide gas.

333. From the volume of nitric oxide obtained, the percentage of ethyl nitrite in the sample employed can be calculated by the following formula, in which *v* represents the number of cubic centimetres of gas obtained ; *p*, the barometric pressure in millimetres ; *e*, the tension of aqueous vapour at the temperature at which the gas is measured ; *d*, the density of the sample (water = 1) ; *n*, the number of c.c. employed ; and *t* the temperature in centigrade degrees :—

$$ENO_2 = \frac{v}{d \times n} \times \frac{p-e}{273+t} \times 0{\cdot}1207.$$

When strictly accurate results are not required, the corrections for pressure, temperature, and tension of aqueous vapour may be omitted, and the calculation much simplified. Thus, if the volume of 0·030 gramme of nitric oxide (representing 0·075 gramme of $C_2H_5NO_2$) under the *ordinary* conditions of pressure and temperature be taken at 23·55 c.c., then

$$\frac{\text{volume of gas in c.c.} \times 0{\cdot}3184}{\text{measure of sample in c.c.} \times \text{density of sample}} = \text{percentage by weight of } C_2H_5NO_2 .$$

334. Eykman's process has a tendency to give results with ethyl nitrite sensibly below the truth, partly, no doubt, from incomplete reaction, but also owing to the solubility of nitric oxide in aqueous liquids. The loss from the latter cause is reduced to a minimum if a nitrometer be employed as recommended, instead of the gas being caused to bubble up through a solution of soda. Probably still closer results might be obtained by saturating the soda solution with common salt.

335. Instead of reducing the ethyl nitrite by means of ferrous sulphate, a solution of potassium iodide may be employed for the purpose. In this case the reaction takes place at the ordinary temperature, and the manipulation is greatly simplified. A nitrometer should be filled with strong brine. 5 c.c. of the sample to be tested should then be placed in the cup of the nitrometer, and allowed to enter through the tap, taking care that no air gets in at the same time. 5 c.c. of a strong solution of potassium iodide is

next allowed to enter, and this is followed by about 5 c.c. of dilute sulphuric acid. Effervescence immediately ensues, and if the tube be vigorously agitated at intervals, the reaction is complete in five to ten minutes, when the level of the liquid in the two limbs of the nitrometer is adjusted, and the volume of nitric oxide gas read off.

If the volume of gas evolved be small, another 5 c.c. of the sample should be let into the nitrometer, and the agitation repeated. The calculation is the same as in Eykman's process, the reaction being $(C_2H_5)NO_2 + KI + H_2SO_4 = (C_2H_5)OH + KHSO_4 + I + NO$.[1] With most specimens of sweet spirit of nitre, a considerable amount of nitric oxide is produced (and iodine liberated) before adding the acid, the reaction probably depending on the presence of free acid in the sample (see footnote on page 145). The results obtained in the nitrometer are remarkably constant, and the method furnishes a very easy means of assaying sweet spirit of nitre with considerable accuracy,[2] which is further increased if a correction of 1·5 c.c. (= 0·0048 gramme of $C_2H_5NO_2$) be made for solubility of the gas.

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[1] The method described in the test has not been published up to the time of going to press. It suggested itself to the author as an improvement on the process of D. B. Dott (see par. 336). It has been proved to give very good results with pure sodium nitrite (prepared from silver nitrite) employed in known amount. The results with spirit of nitrous ether are somewhat higher than those given by Eykman's method, the difference being least when sodium chloride is employed in the latter process and time given for the ferrous solution to react thoroughly on the solution of ethyl nitrite. The results by the iodide method are almost certainly more accurate than those by Eykman's process.

[2] The process has the advantage of great ease and rapidity, and actually measures the nitrous compounds present in the sample, instead of leaving their proportion to be inferred from a more or less complex reaction, such as the reduction of permanganate, &c. The following results were obtained by the author from five typical samples. *No correction* was made for pressure or solubility, the figures representing the actual volumes of gas measured at about 15° C

	Volume of NO from 5 c.c.	Weight of NO from 5 c.c.	$C_2H_5NO_2$ per cent.
	c.c.	milligrammes.	
1. 25°/. Solution in Absolute Alcohol (two months old), ...	29·0 (from 0·5 c.c.)	923·6	22·02
2. Spt. Nitrous Ether, B.P. (two months old), ...	39·4	50·4	2·98
3. Spt. Nitrous Ether, B.P. (age unknown), ...	27·0	34·6	2·63
4. "Spt. Æther Nit. ·850" (new), .	14·7	18·8	1·10
5. "Sp. Æther Nit. Dulc. ·900" (new),	22·0	28·2	1·56

No. 1 was prepared by Mr J. Williams by dissolving 1 part by weight of carefully purified ethyl nitrite in 3 parts by weight of absolute alcohol. The density was 0·8387.

336. D. B. Dott (*Pharm. Jour.*, [3] xv. 492) has proposed to determine ethyl nitrite by treating the liquid with an acidulated solution of potassium iodide, and ascertaining the iodine set free by titration with a standard solution of sodium thiosulphate. If the treatment with potassium iodide be effected in an open basin in presence of air, the amount of nitrite found is liable to be seriously in error, but if air be excluded Dott's method gives fair approximate results, somewhat in excess of the truth. The process can be advantageously employed on the solution which has already been decomposed with potassium iodide in the nitrometer. The nitric oxide is allowed to escape into the air, and the brown liquid is washed into a basin and at once titrated with decinormal thiosulphate. 1 c.c. of this solution (containing 15·8 grammes of $Na_2S_2O_3$ per litre) will react with the iodine liberated by ·0075 grammes of ethyl nitrite.[1]

A useful approximate estimation of the nitrous compounds in spirit of nitrous ether may be made by comparing the depth of the colour developed on adding an acidulated solution of potassium iodide to a known measure of the sample with that of a standard solution of iodine in potassium iodide. Five or ten drops of the sample should be placed in a narrow test-tube, a little water added, and then one or two drops of olive oil, to prevent access of air. An acidulated solution of potassium iodide is then added, and, after five or ten minutes, the colour of the liquid is compared with a standard solution of iodine in the usual way.

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[1] The results obtained in this manner show a constant difference of about 0·005 gramme of nitric oxide above that corresponding to the volume of gas liberated in the nitrometer, the true amount doubtless lying between the two. The difference is most probably due to a small amount of nitric oxide remaining dissolved in the aqueous liquid, which causes the volume of gas to be slightly low, and becoming oxidised to nitrous acid during the subsequent titration liberates a small additional amount of iodine. This source of error becomes very serious if the bulk of the nitric oxide be not previously removed as is done in the nitrometer. Thus, if an attempt be made to determine ethyl nitrite by adding the sample of spirit to an acidulated solution of potassium iodide contained in an open basin, and immediately titrating with standard thiosulphate, the first result is too low, owing to the nitrous ether requiring a sensible time for its decomposition. In a few minutes this error is more than compensated by the additional amount of iodine set free by the nitrous acid produced by the action of the air on the nitric oxide formed in the primary reaction, and this liberation of iodine goes on so rapidly that the stirring necessary to mix the standard solution with the liquid in the basin causes the liquid again to aquire a yellow tinge, which rapidly deepens. If the liquid in the basin be allowed to stand for some time exposed to the air before titrating, the iodine set free often amounts to fully twice the quantity primarily liberated by reaction with the ethyl nitrite present.

337. Various other methods of assaying spirit of nitrous ether have been devised, having for their principle the determination of the real nitrite present. Some of these processes ignore the presence of aldehyde, and others are unsatisfactory for other reasons. Certain of them give fair results in the case of samples of good quality, but are most erratic in their indications when employed for the assay of inferior specimens, and especially those prepared by the London Pharmacopœia process.

338. Muter's process is interesting from the fact that it has been recently employed in the Inland Revenue Laboratory for estimating the nitrous ether contained in commercial sweet spirit of nitre, all the oxidisable matters indicated by the reduction of the permanganate being calculated to their equivalent of ethyl nitrite and reported as "nitrous ether."[1] The following are the details of the process as described by Muter in his original paper (*Analyst*, iv. 125), where he distinctly points out that the results include the reduction due to aldehyde and other oxidisable bodies which may be present, while he has since given the preference to the more recent and accurate method of Eykman. 10 c.c. of the sample should be digested with 2 grammes of potassium hydrate and 10 c.c. of alcohol in a small strong flask, closed by a cork through which passes a bent delivery-tube dipping under the surface of mercury, so that a slight pressure may be maintained on heating the flask. After digestion for about an hour, with frequent agitation, water is added, and the contents of the flask evaporated in a basin till the smell of alcohol is no longer perceptible. The residual liquid is rendered *just neutral* with sulphuric acid, and filtered into a flask containing 75 c.c. of decinormal permanganate (3·162 grammes $KMnO_4$ per litre) previously diluted to 200 c.c. with water and acidulated with 20 c.c. of dilute sulphuric acid (1 in 3). The flask is corked and allowed to stand for half an hour, when excess of a saturated solution of potassium iodide is added, and the liberated iodine titrated with decinormal thiosulphate. The volume of this solution required, deducted from 75, gives the number of c.c. of permanganate decolorised by 10 c.c. of the sample. 1 c.c. of decinormal permanganate oxidises 0·00375 gramme of ethyl nitrite.

By this process, Muter found oxidisable matters equivalent to 2·85 to 3·05 per cent. by weight of ethyl nitrite in samples of spirit of nitrous ether answering strictly to the B.P. tests. With such preparations the method is probably capable of yielding useful comparative results, but in specimens containing much aldehyde, as the preparation of the London Pharmacopœia of 1851 (par. 318), the indications are completely worthless, and should on no account be expressed in terms of nitrous ether.

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[1] In this connection it may be noted that a sample of "sweet spirit of nitre," which was found on independent examination by four different chemists to give but faint indications of ethyl nitrite or other nitrous compounds by the ferrous sulphate colour-test, was, on reference being made to the chemists at Somerset House, certified to contain 1·3 per cent. of nitrous ether.

339. The official process of the United States Pharmacopœia for the estimation of nitrous ether is also based on oxidation, the volume of permanganate said to be decolorised by a spirit of proper strength corresponding to the presence of fully 4 per cent. of nominal ethyl nitrite in the American preparation.[1]

340. Eykman's and the permanganate processes of assaying spirit of nitrous ether estimate the total nitrites present, and fail to distinguish the *ethyl nitrite* from the free *nitrous acid*. As the latter has probably the same therapeutic value as the former, this distinction is rarely important. It may be made, when necessary, by multiplying the free nitrous acid found by titration by 1·6 ($=\frac{75}{47}$) and subtracting the product from the weight of total nitrites calculated as ethyl nitrite. The difference is the true amount of ethyl nitrite. If preferred, the correction may be made by adding some potassium or sodium bicarbonate to a definite quantity of the sample, evaporating to dryness at 100° C., dissolving the residue in water, and estimating the nitrite from the nitric oxide evolved. By deducting the amount thus found, which represents that origin-

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[1] S. P. Sharples of Boston, Mass., has communicated to the author a modification of the U.S. Pharmacopœia process by which an assay of spirit of nitrous ether can be made in about an hour. He does not claim that the process accurately determines the ethyl nitrite, but that it gives constant results with the same sample, which some other of the published methods do not. 10 grammes of the sample are treated with 50 grammes of strong alcoholic potash, and the mixture boiled vigorously for half an hour in a flask furnished with an inverted condenser well supplied with cold water. The contents of the flask are then poured into a porcelain capsule and diluted with 50 c.c. of water, and the liquid kept on the water-bath until the alcohol has evaporated. The solution is then acidified with dilute sulphuric acid, and titrated with decinormal permanganate, the end of the reaction being reached when the colour produced by 1 c.c. persists for a minute. Professor Sharples states that during the winter of 1883–4 he was unable to meet with any spirit of nitrous ether which answered the requirements of the U.S. Pharmacopœia, the average of the apparent ethyl nitrite being not much over 2 per cent. He states that in America there are sold various so-called "concentrated ethers," which are said to contain 90 per cent. and upwards of real ethyl nitrite, but a very small proportion of these distilled at the boiling point of real nitrous ether, and the best of them did not contain more than 60 per cent. of ethyl nitrite, while some contained less than 20 per cent.

ally present as free nitrous acid, from the total, the real nitrous ether may be estimated. (See also par. 335.)

341. The proportion of ethyl nitrite in spirit of nitrous ether B.P., as deduced from the total nitrites, should not fall below 2½ per cent. in a fresh and well-made preparation. In some cases, and especially after keeping, it may fall as low as 2 per cent., but this may be regarded as the minimum limit in a reasonably good preparation. Spirit prepared by the officially obsolete process of the London Pharmacopœia (1851) contains less nitrous ether than the B.P. preparation, and "sweet spirit of nitre" is frequently met with in commerce containing little or no nitrous ether. This is sometimes due to want of care in the distillation, or to the employment of too weak an alcohol, but it is more frequently consequent upon adulteration of the manufactured article by addition of water, with consequent decomposition of the nitrous ether.

342. *Methylated Spirit* is said to be occasionally employed for the preparation of sweet spirit of nitre. The substitution may be detected by agitating 30 c.c. of the sample with 3 or 4 grammes of ignited potassium carbonate, treating 15 c.c. of the decanted dehydrated spirit in a small flask with 10 grammes of anhydrous calcium chloride, attaching a condenser, and heating the flask in boiling water till about 5 c.c. has passed over or scarcely any further distillate can be obtained. The operation proceeds slowly, but requires little attention and should be carried out thoroughly. The contents of the flask are next treated with 5 c.c. of water, and another 2 c.c. distilled. This second distillate is then oxidised by bichromate of potassium and sulphuric acid as described in par. 137, *d*, and the product tested with silver nitrate. If the sample were free from methyl alcohol, the solution darkens, and often assumes transiently a purple tinge, but continues quite translucent; and the test-tube, after being rinsed out and filled with water, appears clean or nearly so. But if the sample contains only 1 per cent. of methylic alcohol (= 10 to 20 per cent. of methylated spirit), the liquid turns first brown, then almost black and opaque, and a film of silver, which is brown by transmitted light, is deposited on the tube. When the sample is methylated to the extent of 3 or 4 per cent. the film is sufficiently thick to form a brilliant mirror. To ensure accuracy the observations should be made by daylight.

343. **Ethyl Chloride.** Hydrochloric ether. "Sweet spirit of salt." C_2H_5Cl.

Ethyl chloride is a fragrant, exceedingly volatile liquid, boiling at 12·2° C., and burning when ignited with a *smoky* green-edged flame, producing fumes of hydrochloric acid. It is sparingly soluble in water, but readily so in alcohol, neither solution giving any precipitate with nitrate of silver. Its solution in an equal volume of alcohol is sometimes employed in medicine. The ether is prepared by distilling alcohol, sulphuric acid, and common salt together, or by passing dry hydrochloric acid gas into absolute alcohol; by adding chloride of zinc to the alcohol, the whole of the latter may be converted into ethyl chloride (*Jour. Chem. Soc.*, xxvii. 636).

344. By the continued action of chlorine on ethyl chloride, a series of substitution-products may be obtained, in which the hydrogen is more or less completely replaced by chlorine. Some of these products are identical with, and others merely isomeric with, similar bodies obtained by other reactions. The following is a list of the products in question :—

Empirical Formula.	Name.	Constitional Formula.	Boiling Point. °C.	Specific Gravity.
C_2H_5Cl	Ethyl chloride; chlorethane, ...	$CH_3.CH_2Cl$	12·2	0·921 at 0°
$C_2H_4Cl_2$	Ethylene Chloride; α-Dichlorethane, (Dutch liquid.) .	$CH_2Cl.CH_2Cl$	84	1·256 at 12
	Ethylidene Chloride; β-Dichlorethane, .	$CH_3.CHCl_2$	60	1·174 at 17°
$C_2H_3Cl_3$	α-Trichlorethane, ...	$CH_2Cl.CHCl_2$	115	1·422 at 17°
	β-Trichlorethane, ...	$CH_3.CCl_3$	75	1·372 at 0°
$C_2H_2Cl_4$	α-Tetrachlorethane, ...	$CHCl_2.CHCl_2$	147	1·614 at 0°
	β-Tetrachlorethane, ...	$CH_2Cl.CCl_3$	127·5	1·530 at 17°
C_2HCl_5	Pentachlorethane, ...	$CHCl_2.CCl_3$	158	1·71 at 0°
C_2Cl_6	Hexachlorethane; Carbon trichloride, . .	$CCl_3.CCl_3$	182	2·00

345. The last product is a crystalline substance identical with that produced by the action of chlorine on Dutch liquid. In the chlorination of ethyl chloride the β-series of isomers are obtained, and these are also produced on a considerable scale in the manufacture of chloral. A very variable mixture of the middle members of the series is an article of commerce under the name of *Liquor anæstheticus*. Another similar mixture, containing the less chlorinated bodies, is the *Æther anæstheticus Aranii*, boiling between 64° and 100° C. The *Æther anæstheticus Wiggers* contains the more highly chlorinated products, and boils between 100° and 140° C.

346. ETHYLIDENE CHLORIDE, CHLORINATED ETHYL CHLORIDE, or β-DICHLOR-ETHANE, $C_2H_4Cl_2 = CH_3.CHCl_2$, is now prepared in a pure state by the action of chlorine on ethyl chloride, or by distilling aldehyde with phosphorus pentachloride. Ethylidene chloride possesses valuable anæsthetic properties, appearing to occupy a position intermediate between chloroform and ether, being safer than chloroform, while a smaller quantity is required than of ether (*Brit. Med. Jour.*, Dec. 18, 1880). It produces

anæsthesia in dogs and rabbits in three or four minutes, but there is no sign of failure of the heart's action. In this respect it differs from chloroform and methylene dichloride, both of which diminish the action of the heart. The isomer of chlorinated ethyl chloride, the dichloride of ethylene or Dutch liquid, produces severe convulsions when its vapour is inhaled.[1] Ethylidene chloride is distinguished by its negative reaction with potassium, whereas Dutch liquid is violently acted on, forming a porous mass and evolving hydrogen and chlor-ethylene, C_2H_3Cl, the latter being a gas of alliaceous odour. The same gas is produced when Dutch liquid is heated with alcoholic potash, while ethylidene chloride is unaffected by the same reagent. The boiling point and density also distinguish Dutch liquid from its isomer. From chloroform, ethylidene chloride is distinguished by its density, boiling point, and negative reaction with Hofmann's test (see par. 425, *a*).

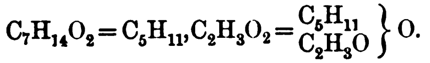
347. Methyl-Chloroform or β-Trichlorethane, $CH_3.CCl_3$, and its isomer $CH_2Cl.CHCl_2$, appear likely to prove valuable as anæsthetics (*Brit. Med. Jour.*, Nov. 13, 1880).

348. **Ethyl Bromide.**[2] Hydrobromic ether. Brom-ethane. C_2H_5Br.

This ether has recently been employed in medicine as a substitute, in certain cases, for chloroform. It boils at 40·7° C., and has a density of 1·419. It burns with difficulty, giving a bright green but smokeless flame, and forming fumes of hydrochloric acid. The boiling point and smokeless flame distinguish it from ethyl chloride.

Ethyl bromide is liable to contain an admixture of ordinary ether, which reduces the specific gravity. Some samples are contaminated with an acrid impurity, of extremely unpleasant alliaceous odour, and less volatile than pure ethyl bromide. Such specimens are unfit for medicinal use.

349. **Amyl Acetate.** Acetate of pentyl.



$$C_7H_{14}O_2 = C_5H_{11},C_2H_3O_2 = \left.\begin{matrix} C_5H_{11} \\ C_2H_3O \end{matrix}\right\} O.$$

Amyl acetate is prepared by distilling amyl alcohol with an acetate and sulphuric acid. When pure, it is a colourless liquid having an exceedingly fragrant odour. It is insoluble in water, but soluble in all proportions in ether, amyl alcohol, and ordinary alcohol. The last solution constitutes the essence of jargonelle pear of commerce. Amyl acetate boils at 137° C., and has a density of ·8763 at 15° C.

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[1] A similar difference is observable between the action of butyl chloride and that of its isomer iso-butyl chloride.

[2] On the preparation and characters of ethyl bromide, see *Pharm. Jour.*, [3] x. 9, 962; xi. 3.

Amyl acetate has recently been proposed as a suitable liquid to burn in a standard lamp for photometric purposes.

350. Amyl acetate may be determined by the general method in par. 291. From *alcohol* it may be separated by agitating the liquid with an equal measure of saturated solution of chloride of calcium, which dissolves the alcohol only.

Any admixture of *amyl alcohol* may be separated and determined approximately by treating the sample in a graduated tube with a mixture of equal volumes of glacial acetic acid and water.

This dissolves amyl alcohol, but leaves the amyl acetate insoluble (together with any valerate or pelargonate of amyl which may be present). By first separating the ethyl alcohol by salt water, or petroleum spirit, as described in pars. 268 and 269, this method may be applied to the essence of jargonelle pear.

351. **Amyl Nitrite.** $C_5H_{11}NO_2 = \left.\begin{matrix}(C_5H_{11})\\(NO)\end{matrix}\right\}O.$

Amyl nitrite is prepared by processes similar to those employed for obtaining nitrite of ethyl, amyl alcohol being substituted for spirit of wine. To obtain a product fit for medicinal use, the amyl alcohol should be carefully purified, and have a boiling point of 129° to 132° C. By passing nitrous acid gas (best prepared by the reaction of nitric acid on arsenious oxide) into this alcohol, a very pure nitrite is obtained. After washing the product with water and solution of carbonate of sodium, the oily liquid is rectified, the fraction passing over between 90° and 100° C. being retained. By carefully refractionating the distillate with a dephlegmator (par. 35) a very pure product may be obtained, but it must be again washed with sodium carbonate to separate traces of acid produced by decomposition of the ether during redistillation.[1]

352. Pure amyl nitrite has a density of 0·877, and is said to boil constantly at about 96° C., though on this point there are conflicting statements (see *Pharm. Jour.*, [3] ix. 899, and x. 231). It has a yellowish colour, penetrating apple-like odour, pungent aromatic taste, and produces a very powerful effect on the system

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[1] Nitrite of amyl is sometimes said to give an orange-yellow vapour, but this phenomenon is due to the liberation of oxides of nitrogen. These are commonly assumed to be produced by decomposition of the amyl nitrite, but E. T. Chapman states their production to be due to the ready solubility of nitric oxide in amyl nitrite and its evolution on heating.

when its vapour is enhaled. It burns, when ignited, with a fawn-coloured smoky flame.

Amyl nitrite is insoluble in water, but soluble in alcohol in all proportions. It also dissolves in amyl and methyl alcohols, in glacial acetic acid, and is miscible in all proportions with ether, chloroform, carbon disulphide, benzene, petroleum spirit, and oils.

In contact with the air, and apparently more readily under the influence of light, amyl nitrite develops an acid reaction owing to partial decomposition. Probably this change occurs more readily in presence of moisture.

353. Concentrated sulphuric acid attacks amyl nitrite with great energy, red fumes being evolved, and a black, foul-smelling liquid formed. Occasionally the mixture inflames.

354. A characteristic test for amyl nitrite is the formation of potassium valerate when the liquid is dropped on fusing caustic potash.

355. When gently warmed with excess of an aqueous solution of caustic potash, potassium nitrite is formed, and a stratum of amylic alcohol floats on the surface of the liquid. The change occurs more readily by using alcoholic potash and subsequently adding water to cause the separation of the amylic alcohol. On removing the aqueous liquid, acidulating it with acetic acid, and adding potassium iodide, the nitrite will occasion an abundant liberation of iodine.

356. When amylic nitrite is distilled slowly with methyl alcohol it is completely decomposed, with formation of amyl alcohol and methyl nitrite. Ethyl alcohol causes a less complete change, but it is evident that a spirituous solution of amyl nitrite would be liable to undergo decomposition.

357. Commercial Amyl Nitrite.

The amyl nitrite commonly met with is sometimes far from pure, being liable to contain ethylic and amylic alcohols, amyl nitrate, nitrites of butyl and hexyl, nitropentane, valeric aldehyde, water, and other impurities. If the amyl nitrite be prepared in the manner directed in par. 349, most of these bodies will be present in but very insignificant proportion, but the contrary is the case if impure fusel oil be substituted for carefully purified amylic alcohol, or if the latter be converted by treatment with nitric acid instead of nitrous acid, as is done by some manufacturers.[1]

358. The following table shows the composition, densities, and

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[1] The use of nitric acid is certain to result in the formation of much valeric aldehyde and more or less amyl nitrate, and the boiling point of the former of these bodies precludes the possibility of subsequently separating it by fractionating the crude product.

boiling points of the more important bodies likely to be present in impure commercial nitrite of amyl:—

Name.	Formula.	Specific Gravity.	Boiling Point ° C.
Nitropentane, . . .	$C_5H_{11}(NO_2)$	·877	150–160
Amyl nitrite, . . .	$C_5H_{11}.O.NO$	·902 at 0°C.	96
Amyl nitrate, . . .	$C_5H_{11}.O.NO_2$	1·000 at 7°	148
Amyl alcohol, . . .	$C_5H_{11}.O.H$	·814 at 15°	128–131
Valeric aldehyde, . .	$C_4H_9.CO.H$	·8057 at 17°	92·5

359. From these data it is evident that any valeric aldehyde in the crude product will not be likely to be removed by fractional distillation, though the other impurities can be more or less perfectly eliminated by such treatment. Any admixture of valeric aldehyde or amylic alcohol will tend to reduce the specific gravity of the preparation, while amyl nitrate acts in a contrary manner. As, however, the last body has a comparatively high boiling point, a very instructive examination of commercial amyl nitrite can be made by distilling the sample with a dephlegmator, and noting the volumes, densities, and odours of the fractions collected at different temperatures. A fairly pure article, when fractionally distilled in this manner, will yield fully 80 per cent. of its original measure between 90° and 100° C., and should leave no very considerable residue at the latter temperature. Some specimens have been found to boil at temperatures ranging from 70° to 180°, and occasionally to leave a residue at 220° C.[1] As a rule, incomplete distillation at 100° is due chiefly to the presence of amyl alcohol, heavy traces of which may apparently be formed by partial decomposition of the nitrite during distillation. Hence

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[1] The data given in the test respecting the results of fractionating commercial amyl nitrite are based chiefly on the observations of D. B. Dott and W. H. Greene (*Pharm. Jour.*, [3] ix. 172, 899; x. 231), but they are wholly at variance with the experience of E. R. Squibb (*Ephemeris*, ii. 707; and *Pharm. Jour.*, [3] xv. 485), who has fractionated three typical specimens of American amyl nitrite. The purest of these samples gave only 19·2 per cent. by measure of distillate at 95° C., and 45·6 at 100°, a total of 90·2 per cent. distillating below 128°. The distillation was conducted in an ordinary retort with the bulb of the thermometer immersed in the liquid, whereas in the experiments of Dott and Greene, a flask with a dephlegmating tube was used. These differences in the mode of manipulation would materially affect the proportions of the distillate obtained at a particular temperature, but Squibb's results still point to the presence of much besides amyl nitrite in the samples examined by him.

commercial amyl nitrite of good quality may leave a residue of 5 to 10 per cent. at 100°.

360. A further examination of the nature of the 90° to 100° fraction might be made by gently heating it for some time with methyl alcohol in a flask furnished with an inverted condenser. On subsequent distillation, the fraction passing over between 90° and 100° will consist mainly of the *valeric aldehyde* of the original sample, the amyl nitrite having been converted into amyl alcohol and the very volatile methyl nitrite.

361. *Nitropentane*, $C_5H_{11}NO_2$, a body isomeric with amyl nitrite, appears to be present in most commercial specimens of the latter, and sometimes in notable quantity. It may be detected by subjecting the fraction distilling between 140° and 170° C. to the action of nascent hydrogen, when amylamine, $C_5H_{11}NH_2$, will be formed, and may be recognised by the alkaline character of the distillate obtained on boiling with caustic potash. Nitropentane may also be detected by dissolving the 140° to 170° fraction in solution of caustic potash, adding a little sodium nitrite, and then dilute sulphuric acid very cautiously, when a blood-red coloration will be produced, which disappears when the solution becomes acid. The pentyl-nitrolic acid produced may be extracted by agitation with ether. Probably the test might be applied by warming the original sample with alcoholic potash and cautiously adding dilute sulphuric acid.

362. *Amyl Nitrate*, $C_5H_{11}NO_3$, if present, will be contained in the last fractions obtained on distilling a sample of amyl nitrite. There is no simple direct test for its presence, and D. B. Dott states that he has failed to detect it in cases where he made a special search for it.

363. *Valeric Aldehyde*, $C_5H_{10}O$, may be detected by treating the sample with three measures of a mixture in equal parts of strong ammonia and absolute alcohol, then adding a few drops of nitrate of silver solution and warming gently, when a dark brown coloration will be produced if valeric aldehyde be present.

364. *Butyl* and *Hexyl Compounds* may be detected by saponifying the sample with caustic potash and examining the amylic alcohol layer for butyl and hexyl alcohols by distillation, &c., as indicated in par. 267.

365. *Free Acid* may be detected and determined as in spirit of nitrous ether (par. 326) after dissolving the sample in rectified spirit. The United States and German Pharmacopœias agree that the free acid in 10 c.c. of amyl nitrite should be wholly neutralised by agitation with 2 c.c. of a mixture of 1 measure of ammonia of ·950 sp. gr. and 9 parts of water.

366. *Hydrocyanic Acid*, occasionally present as a by-product, may be recognised by largely diluting the sample with alcohol and adding silver nitrate, when white curdy silver cyanide will be precipitated.

367. The *real Amyl Nitrite* present in a commercial sample might probably be determined by saponifying the sample with alcoholic potash and treating the product by Eykman's or Dott's process (para. 331, 336).

368. *Water* increases the specific gravity of the preparation, and renders it turbid when cooled to the melting point of ice. The presence of water increases the tendency to decomposition.

369. **Artificial Fruit Essences.**—The natural bouquets and flavours of fruits have been found to depend, in many instances, on the presence of small quantities of certain ethers, and these bodies are now prepared on a very extensive scale for the imitation of the natural flavours.

The following is a list of the natural odours and flavours of fruits, &c., which can be almost exactly simulated by unmixed products of artificial origin:—

Natural Odour or Flavour.	Simple Artificial Body.
Bitter almond ; Peach.	Nitro-benzene ; Benzoic aldehyde.
Jargonelle Pear.	Amyl acetate.
Apple.	Amyl valerate.
Quince.	Ethyl pelargonate.
Pine-apple.	Ethyl butyrate.
Melon.	Ethyl sebate.
Greengage.	Ethyl œnanthylate.
Mulberry.	Ethyl suberate.
Gaultheria procumbens.	Methyl salicylate.
Spirea ulmaria.	Salicylic aldehyde.

370. The following table, compiled from the recipes of J. H. Maisch, shows the composition of various artificial fruit-essences and flavours employed in practice. The numbers given indicate the number of measures of the ethers, &c., to be added to each 100 measures of rectified spirit. The chloroform and aldehyde can be omitted in most cases without serious detriment to the flavour. To make the essences of orange and lemon, 10 parts of the respective essential oils must be employed in addition to the ingredients given in the table. In cases in which acids are employed, the figures refer to volumes of a cold saturated solution of the acid in alcohol of ·830 specific gravity :—

	Pine-apple.	Melon.	Strawberry.	Raspberry.	Currant.	Grape.	Apple.	Pear.	Cherry.	Plum.	Apricot.	Peach.	Orange.	Lemon.	Banana.
Chloroform . .	1	...	...	...	...	2	1	...	...	...	1	...	2	1	...
Aldehyde . .	1	2	...	1	1	2	2	...	...	5	...	2	2	2	...
Methyl salicylate .	...	...	1	1	...	1	...	...	...	...	...	...	1	...	...
Ethyl nitrite . .	...	...	1	1	...	...	1	...	...	...	...	...	...	1	...
,, formate .	...	1	1	1	...	2	...	...	...	1	...	5	1	...	...
,, acetate .	...	...	5	5	5	...	1	5	5	5	...	5	5	10	...
,, butyrate .	5	4	5	1	...	...	...	...	...	2	10	5	1	...	10
,, valerate .	...	5	...	...	...	...	...	...	...	...	5	5	...	...	...
,, pelargonate .	...	...	...	1	1	10	...	...	1	...	1	...	...	...	...
,, benzoate .	...	...	...	1	1	...	...	...	5	...	...	...	1	...	...
,, sebate .	...	10	...	1	...	...	...	...	...	...	...	1	...	...	...
Amyl alcohol .	...	...	...	...	...	...	...	...	...	...	2	2	...	...	...
,, acetate .	...	...	3	1	...	...	...	2	...	...	...	...	1	...	10
,, butyrate .	10	...	2	1	...	...	...	...	...	...	1	...	...	...	...
,, valerate .	...	...	...	...	...	...	10	...	...	...	...	...	...	...	...
Tartaric acid . .	...	...	...	5	5	5	...	...	...	...	1	...	1	10	...
Oxalic acid . .	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...
Succinic acid . .	...	...	...	1	1	3	...	...	...	...	...	...	...	1	...
Benzoic acid . .	...	...	...	...	1	...	...	...	1	...	...	...	...	...	...
Glycerin . .	3	3	2	4	...	10	4	2	3	8	4	5	10	5	...
Peach oil (benzoic aldehyde) .	...	...	...	...	...	...	...	...	...	4	...	5	...	...	...

The colour of strawberry and raspberry essences is communicated by aniline-red mixed with a little caramel.

The true strength and flavouring powers of fruit-essences is best ascertained by noting their taste and odour after copious dilution with water. For examination of the ethers, the sample should be treated with dry calcium chloride, which will unite with the alcohol, and the ethers may generally be distilled off.

371. ALDEHYDES.

The aldehydes are a series of compounds intermediate in composition between the alcohols and their corresponding acids. Those corresponding to the monatomic alcohols of the ethyl series may be expressed by the general formula—

$$C_nH_{2n}O = C_nH_{2n-1}O.H = C_mH_{2m+1}.CO.H\,.$$

372. Aldehydes result from the treatment of the corresponding alcohols by oxidising agents of moderate power, such as dilute nitric acid or dilute chromic acid mixture used cautiously. They are also formed by distilling a mixture of the sodium or calcium salt of the corresponding acid with the similar compound of the acid next lowest in the series, thus :—

$$\underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Sodium formate.}}{NaCHO_2} = \underset{\text{Acetaldehyde.}}{C_2H_4O} + \underset{\text{Sodium carbonate.}}{Na_2CO_3}$$

Aldehydes may also be obtained by the action of nascent hydrogen on the chlorides of the corresponding acid radicles, and by various other reactions.

373. When pure, the aldehydes may apparently be preserved without change, but the presence of mere traces of impurity (*e.g.*, mineral acids), tends to cause their gradual conversion into polymers or condensation-products, in the latter case one or more molecules of water being simultaneously eliminated.

374. By oxidation, the aldehydes are very readily converted into the corresponding acids. Hence, they are powerful reducing agents, precipitating metallic silver from the ammonio-nitrate, decolorising permanganate, &c.

375. By the action of nascent hydrogen (sodium amalgam), the aldehydes are reduced to the corresponding alcohols, but the fixation of hydrogen is often attended with condensation, and consequent co-formation of a higher diatomic alcohol.

376. When heated with solutions of caustic alkalies, the aldehydes are mostly converted into resinous bodies which are probably condensation-products. By fusion with caustic potash, aldehydes are converted into the potassium salts of the corresponding acids, hydrogen being simultaneously evolved; in some cases this acts on another portion of the aldehyde and converts it into the corresponding alcohol; thus:—

$$\underset{\substack{\text{Benzoic}\\\text{aldehyde.}}}{2C_7H_6O} + KHO = \underset{\substack{\text{Potassium}\\\text{benzoate.}}}{KC_7H_5O_2} + \underset{\substack{\text{Benzylic}\\\text{alcohol.}}}{C_7H_8O}$$

Many of the aldehydes form compounds with water, hydrochloric acid, &c., but the products are very unstable.

377. The aldehydes readily combine with ammonia, the products first formed often undergoing molecular condensation more or less rapidly. The ammonia-compounds of the aldehydes of the acetic series are not liable to this change, and are stable crystalline bodies which liberate the original aldehyde on treatment with dilute sulphuric acid.

378. A reaction peculiar to the aldehydes and allied bodies (ketones), and common to all members of the class, is the property of forming stable crystalline compounds with the acid sulphites of the alkali-metals. The sodium compound is readily obtained on treating the aldehyde or its aqueous solution with excess of a saturated cold solution of acid sulphite of sodium, when the compound separates in crystals which are soluble in water or alcohol, but insoluble in a strong solution of acid sulphite of sodium. From this compound the aldehyde may be regenerated by treatment with dilute sulphuric acid (or sodium carbonate), or sometimes by simply warming the aqueous solution.

379. Aldehydes of the acetic series (as also chloral) reduce hot Fehling's solution, but aldehydes of the aromatic series do not.

380. All bodies of the aldehyde class give a violet coloration with an acid solution of rosaniline previously mixed with sufficient sodium sulphite almost to decolorise it.[1]

381. A mere trace of most bodies of the aldehyde class produces a fine scarlet colour with a solution of phenol in excess of sulphuric acid, the colour changing to a dark red on warming the mixture.

382. A delicate test for aldehydes is the violet-red colour they give with diazobenzene-sulphonic acid in presence of free alkali (*Ber.*, xvi. 657). 1 part of freshly-prepared diazobenzene-sulphonic acid is dissolved in 60 parts of cold water rendered alkaline by caustic soda. To this solution is added the liquid to be tested (previously mixed with dilute solution of caustic soda) together with a little sodium amalgam. If an aldehyde be present, an intense violet-red coloration is produced, either immediately or within 20 minutes. The colour is destroyed by long exposure to the air, and is changed by the addition of an acid.

The reaction is readily yielded by a solution containing 1 part in 3000 of benzoic aldehyde (oil of bitter almonds), and has been obtained with acetic, valeric, and œnanthic aldehydes, as also with furfuraldehyde and glyoxal. Chloral and benzoïn do not give the reaction. Acetone and ethyl aceto-acetate give a red colour, but without the violet tint characteristic of an aldehyde. The reaction is not produced by phenol, resorcinol, or pyrocatechol (if care be taken to have excess of alkali present), but is given by glucose. It is said to be more delicate than that with rosaniline reduced with sulphurous acid; but the reaction is more especially suitable for the detection of aldehydes which are permanent in alkaline solutions.

383. E. Fischer recommends the employment of phenylhy-

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[1] Examined as described in the text, acetaldehyde, paraldehyde, and propionaldehyde give an intense red-violet coloration. Chloral gives at once a fine colour, but chloral hydrate gives no reaction. Acroleïn and butyl chloral produce a violet colour on shaking. Furfurol and benzaldehyde give the colour more readily. Salicylic and cuminic aldehydes react well after some agitation. Cinnamic aldehyde and furfur-acroleïn give at first an intense yellow colour, soon changing to violet-red. Acetone readily reacts on shaking, but acetophenone and benzophenone have no action. Methyl and ethyl alcohols give a faint violet colour on shaking, propylic and isopropylic alcohols a scarcely perceptible reaction, while with their higher homologues, and phenols, glycols, quinine, sugars, and formic acid, no colour whatever is obtained.

drazine hydrochloride as a reagent for detecting bodies of the aldehyde class (*Ber.*, xvii. 573; *Jour. Soc. Chem. Ind.*, iii. 330).

384. *Acroleïn*, *Valeral*, *Furfurol*, and the *Essential oils* of bitter almonds, cinnamon, cloves, cumin, and meadowsweet have the constitution and characters of aldehydes. All these form crystalline compounds with the acid sulphites of the alkali metals.

Acetone (par. 126) and *Acetal* (par. 400) are bodies allied to the aldehydes, and *Chloral* (par. 401) is a trichlor-aldehyde.

385. **Formic Aldehyde.** Formaldehyde. Methaldehyde. CH_2O.

This body is produced by the limited oxidation of methyl alcohol. Its formation is probably the first stage towards the production of carbohydrates, &c., in plants, by the deoxidation of carbonic acid. Formic aldehyde presents a general resemblance to ordinary or acetic aldehyde, but it is polymerised with extreme readiness. It is gaseous at the ordinary temperature, and hitherto has not been obtained pure, though its polymer para-formaldehyde, $C_3H_6O_3$, is a white insoluble body, subliming at the temperature of boiling water, and suffering de-polymerisation at a higher temperature, or when heated to 140° with excess of water in a sealed tube.

Formaldehyde may be determined by treatment with excess of standard ammonia, which converts it into hexamethylene-amine, thus:—$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$. The excess of ammonia may be titrated with standard acid, or the resultant hexamethylene-amine may be weighed. When heated on the water-bath for several days with caustic soda, formaldehyde yields sodium formate and methyl alcohol, and the reaction may be employed quantitatively as described in par. 291.

386. **Acetic Aldehyde. Acetaldehyde.** Ethylidene Oxide.

$$C_2H_4O = C_2H_3O,H = C\left\{\begin{array}{l} H \\ H \\ H \\ CO.H. \end{array}\right.$$

This is the body from which the class of aldehydes derived their name, and when the word aldehyde is used as a proper name without qualification, ordinary or acetic aldehyde is always understood.

387. In constitution, aldehyde is intermediate between ethyl alcohol and acetic acid; thus—

Ethyl alcohol, $C_2H_6O = C_2H_5.OH = CH_3.CH_2.OH.$
Aldehyde, $C_2H_4O = C_2H_3.OH = CH_3.CO.H.$
Acetic acid, $C_2H_4O_2 = C_2H_3O.OH = CH_3.CO.OH.$

388. Many of the properties of acetaldehyde common to other bodies of the class are described on pages 164 and 165.

389. Aldehyde results from the destructive distillation of various organic compounds, and from the limited oxidation of alcohol by dilute chromic acid, nitric acid, air in presence of platinum black, &c. In practice, aldehyde is prepared by distilling together alcohol, sulphuric acid, and manganese dioxide, but it may be obtained in various other ways.

390. Acetic aldehyde is a mobile, colourless liquid, having a pungent suffocating odour. In pure samples, the disagreeable odour is much less marked than in the crude substance. Its density is ·790, and it boils at 22° C. It does not redden litmus, either when absolute or when in solution; but turns acid on exposure to air, from oxidation to acetic acid, which change occurs with great facility.

Acetic aldehyde is miscible in all proportions with water, alcohol, and ether. It is insoluble in a saturated solution of calcium chloride, but this fact is not of service for the quantitative separation of aldehyde from alcohol. A better method of separation is to treat the liquid with dry calcium chloride, which forms a compound with the alcohol, when the aldehyde may be distilled off by the heat of a water-bath.

391. When kept in closed vessels, aldehyde often becomes converted into liquid or solid polymeric modifications, especially in presence of traces of mineral acid or certain other impurities. The alcoholic solution of aldehyde is tolerably permanent. Oxidising agents convert aldehyde into acetic acid. Dehydrating agents, such as phosphoric anhydride and concentrated sulphuric acid, when heated with aldehyde turn it thick and black; but aldehyde may be distilled from sulphuric acid diluted with an equal weight of water.

392. Aldehyde is a powerful reducing agent. It separates metallic silver from the ammonio-nitrate, when gently warmed, while acetate is formed in the liquid. The reaction is rendered more delicate by the addition of caustic alkali. A suitable mixture may be prepared by mixing equal measures of 10 per cent. aqueous solutions of silver nitrate and caustic soda, and then adding ammonia drop by drop till the oxide of silver is dissolved.[1] This reagent yields an immediate mirror with a liquid containing 1 per cent. of aldehyde, and in half a minute with a solution containing 1 in 1000, while 1 part of aldehyde in 10,000 of water yields a yellow-brown mirror in five minutes. The solution to be tested

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[1] The reagent should be freshly prepared, as it is liable to decompose with deposition of fulminating silver.

should be previously distilled, as several varieties of sugar slowly reduce the reagent.

393. Aldehyde gives a copious precipitate of red cuprous oxide when heated with Fehling's solution. Neither this reaction nor that with silver solution appears to be applicable for its quantitative determination.

394. When in alcoholic or aqueous solution, aldehyde is conveniently detected by its reaction on heating with caustic alkali. When thus treated, the liquid becomes yellow and turbid, and a reddish-brown resinous mass rises to the surface, the liquid emitting a highly disagreeable odour. The solution contains a formate and acetate of alkali metal. This formation of the aldehyde-resin is the most characteristic reaction of aldehyde, and has been utilised by J. C. Thresh (*Pharm. Jour.*, [3] ix. 409), for its approximate determination. To effect this, 1 part of pure aldehyde should be diluted with 200 measures of water, 30 measures of a syrupy solution of caustic soda added, and the whole heated and kept at the boiling point for a few seconds. It is then allowed to cool, and after two hours is diluted with 200 measures of warm methylated spirit (free from aldehyde), and then made up to 500 measures by addition of water. This solution is quite clear, and of a reddish-yellow colour. As it quickly alters, it is desirable to make a solution of bichromate of potassium of the same tint, and employ that instead of the original liquid. To determine aldehyde, the liquid containing it, suitably diluted and previously distilled if necessary, is treated in exactly the same manner as the pure aldehyde, and the colour of the liquid obtained compared with the standard, and the darker diluted with water till the tints are identical. The comparison is affected in much the same manner as in Nessler's method of determining ammonia.

395. A characteristic property of aldehyde, but common to all bodies of the class, is the formation of white crystalline compounds with the acid sulphites of the alkali metals. Thus :—$C_2H_3OH + NaHSO_3 = Na(C_2H_3)SO_3 + H_2O$. These compounds are more or less soluble in alcohol and water, but insoluble in strong solutions of the acid sulphites. Hence, by adding excess of acid sodium sulphite to an aqueous solution of aldehyde, the latter substance may be entirely separated as sodium ethylidene sulphite, and can be obtained in a free state by distillation with a dilute mineral acid or an alkaline carbonate.

396. Aldehyde also combines with ammonia, forming a crystalline substance of the formula C_2H_4O,NH_3, or $CH_3.CH(NH_2).OH$ (amido-ethylic alcohol), insoluble in ether and decomposed on distillation with moderately dilute sulphuric acid.

397. **Paraldehyde.** $C_6H_{12}O_3$.—This solid polymeride of acetaldehyde is produced by adding a minute quantity of hydrochloric or sulphurous acid to ordinary aldehyde. Also, on adding a drop of concentrated sulphuric acid to aldehyde violent ebullition occurs, much aldehyde is volatilised, and the residue consists of paraldehyde. Zinc chloride acts similarly, but calcium chloride and potassium acetate do not. The paraldehyde may be purified from unchanged aldehyde by cooling the liquid below 0°, when the crystals which separate are pressed between folds of blotting paper and distilled.

398. Paraldehyde is a colourless liquid, solidifying at 10° C. and boiling at 124°. The density is 0·998 at 15°. It has a pleasant ethereal odour, is soluble in 8½ measures of cold water, and in all proportions of alcohol and ether. It may be distilled alone without change, but if a small proportion of zinc chloride or sulphuric or hydrochloric acid be present the operation reconverts it into ordinary aldehyde.

Paraldehyde is employed in medicine as a substitute for chloral, over which it presents some advantages, but has a persistent and acrid after-taste. Some commercial specimens are very impure.

399. **Metaldehyde,** xC_2H_4O, is another polymeride produced simultaneously with paraldehyde (see par. 397). It is insoluble in water, and almost insoluble in alcohol or ether, but dissolves somewhat in acetaldehyde. Its best solvents are hot chloroform and benzene. At ordinary temperatures the crystals are permanent in the air. It is reconverted more or less completely into ordinary aldehyde by repeated distillation, or by heating in a sealed tube to 110° to 115°, and readily by distillation with a little dilute sulphuric acid. Permanganate, chromic acid mixture, and ammonia are without effect on metaldehyde, but chlorine at once converts it into ordinary chloral. With a hot strong solution of caustic potash or soda metaldehyde very slowly yields aldehyde-resin, the reaction being probably preceded by a formation of ordinary aldehyde.

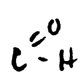
400. **Acetal,** $C_6H_{14}O_2$, has the constitution of a di-oxyethyl-acetaldehyde :—$CH_3.CH(OC_2H_5)_2$. It is produced by the action of aldehyde on alcohol, and hence is a constituent of crude spirit and of the "faints" obtained in the rectification of alcohol. When pure, acetal is a liquid of pleasant taste and odour, boiling at about 105° C. and having a density of ·821 at 22° C. By oxidising agents it is converted into acetic acid and aldehyde, and when heated with acetic acid, it yields ethyl acetate and aldehyde. If a dilute aqueous solution be treated with caustic soda and iodine a clear colourless liquid is formed, which yields a dense precipitate of iodoform when acidified. From alcohol, acetal may be separated

by distillation over dry chloride of calcium, and from aldehyde and ethyl acetate by heating the liquid with strong solution of potash.

Dimethyl-acetal occurs in crude wood spirit (par. 116), in proportions varying from 1 to 2 per cent.

401. CHLORAL.

Trichlor-aldehyde. $C_2HCl_3O = CCl_3.CO.H$.



Chloral is obtained in practice by the prolonged action of dry chlorine on absolute alcohol. When the liquid possesses a density of 1·400 it is distilled with an equal weight of strong sulphuric acid, the fractions passing over below 94° being kept separate, and the process stopped when the temperature rises to 100° C. The distillate is neutralised with chalk and again distilled. The reactions which occur in the manufacture of chloral are very complicated, and various secondary products are formed.[1]

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[1] The action of chlorine on absolute alcohol results in the formation of aldehyde and acetal, thus:—$C_2H_6O + Cl_2 = C_2H_4O + 2HCl$; and $C_2H_4O + 2C_2H_6O = C_2H_4(C_2H_5O)_2 + H_2O$. By the continued action of chlorine, that element replaces three atoms of hydrogen, forming trichlor-acetal, $C_2HCl_3(C_2H_5O)_2$, which may be regarded as a compound of chloral with ether, $C_2HCl_3O,(C_2H_5)_2O$. By reaction with the generated hydrochloric acid this yields chloral alcoholate, C_2HCl_3O,C_2H_6O, and ethyl chloride, C_2H_5Cl. Most of the latter reacts with the alcohol present to form ether, which is converted by fresh chlorine step by step into mono-, di- tri-, and tetra-chlorinated ether.

During the subsequent distillation with concentrated sulphuric acid, the tetra-chlorinated ether and the chloral alcoholate split up into chloral and ethyl-sulphuric acid, as follows:—

$$C_2H_5.O.C_2HCl_4 + H_2SO_4 = HCl + C_2HCl_3O + (C_2H_5)HSO_4$$

and

$$C_2HCl_3O,C_2H_5HO + H_2SO_4 = H_2O + C_2HCl_3O + (C_2H_5)HSO_4.$$

The ethyl-sulphuric acid reacts with hydrochloric acid to form sulphuric acid and ethyl chloride, $(C_2H_5)HSO_4 + HCl = H_2SO_4 + (C_2H_5)Cl$.

By the continued action of chlorine on tetra-chlorinated ether, a penta-chlorinated ether ($C_2H_5.O.C_2Cl_5$) is produced. This body has a density of 1·65, and does not yield chloral when treated with sulphuric acid. Hence, in practice, the current of chlorine gas is interrupted when the liquid has reached a density of 1·40.

By reacting on the ethyl chloride formed in the process, chlorine produces a whole series of chlorinated substitution-products (see par. 344).

By the chlorination of two associated molecules of aldehyde, a substance called butyl-chloral is formed, having the formula $C_4H_5Cl_3O$. It is distinguished from ordinary chloral by its boiling point and the melting point of its hydrate, as well as by the mode of its decomposition by alkalies (see par. 428 *et seq.*).

The occurrence of many or all of the above reactions sufficiently accounts

402. Anhydrous chloral is a thin colourless oily liquid, of a density of 1·544 at 0°, or 1·502 at 18° C. It boils at 94°·4 and distils unaltered. It is soluble in ether or chloroform without change.

403. When kept for some time, or when left in contact with moderately concentrated sulphuric acid, chloral is converted into an insoluble polymeric modification called metachloral, $C_6H_3Cl_9O_3$, which is insoluble in cold and but sparingly soluble in boiling water, and insoluble in alcohol or ether even when boiling. When perfectly pure, anhydrous chloral does not become polymerised, and the change is also said to be prevented by addition of a little chloroform. When heated to 180° metachloral distils with reversion to liquid chloral.

404. By the action of aqueous alkalies chloral yields chloroform and a formate, thus:—

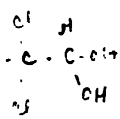
$$CCl_3.COH + KO.H = KO.COH + CCl_3.H.$$

405. If an aqueous solution of chloral be heated to 50° C. with zinc, and very dilute acid gradually added, aldehyde and para-aldehyde are formed and may be distilled off. $C_2HCl_3O + H_6 = 3HCl + C_2H_4O$.

When chloral is mixed with an equivalent quantity of absolute alcohol it is converted into

406. **Chloral Alcoholate.** $C_4H_7Cl_3O_2 = C_2HCl_3O,C_2H_6O$. This substance forms white crystals, which melt at 46° C. It boils at 113°·5 C. (see par. 410). These properties, amongst others, distinguish it from

407. **Chloral Hydrate.** Trichlor-ethylidene glycol. $C_2H_3Cl_3O_2 = C_2HCl_3O,H_2O = CCl_3.CH(OH)_2$.



This important substance results from the mixture of equivalent quantities of anhydrous chloral and water. The mixture becomes heated and solidifies to a mass of crystals of the hydrate. Chloral hydrate is soluble in 1½ times its weight of water. It is also soluble in alcohol, ether, benzene, petroleum spirit, and carbon disulphide. When crystallised from the last solution it boils at 97°·5 C.

408. When mixed with an equal weight of camphor or carbolic acid chloral hydrate rapidly liquefies. The liquid smells of both its constituents, and does not precipitate nitrate of silver.

409. Chloral hydrate is soluble with difficulty in cold chloro-

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for the variety of the impurities sometimes contained in commercial chloral hydrate and chloroform. The distinction between the different chlorinated oils, and their recognition in chloroform, chloral, &c., can at present be effected but very imperfectly.

form, requiring four times its weight, a fact which distinguishes it from the alcoholate, which is readily soluble in chloroform. The distinction of chloral hydrate from chloral alcoholate is important, as the latter is said to have been substituted for the former. The alcoholate contains a smaller percentage of chloral than the hydrate, and its physiological effect appears to be different.

410. In the following table are given other useful distinctions between chloral alcoholate and chloral hydrate :—

	Chloral Alcoholate.	Chloral Hydrate.
1. Melting point.	46° C.	48°–49° C.
2. Boiling point.	113·5° C.	97·5° C.
3. Density of the fused substance at 66° C.	1·344	1·57
4. Sp. gr. of the aqueous solution at 15·5° C.		
5 per cent.	1·007	1·019
10 ,,	1·028	1·040
15 ,,	1·050	1·062
20 ,,	1·071	1·085
5. Gently heated with nitric acid of 1·2 sp. gr.	Violently attacked.	Scarcely acted on.
6. Shaken with an equal volume of strong sulphuric acid.	Brown coloration.[1]	No visible change.[1]
7. Warmed with two volumes of water.	Melts without complete solution, and on cooling congeals below the surface.	Readily dissolved.
8. Heated on platinum foil.	Inflames readily.	Scarcely burns.
9. With alkali and iodine.	Gives iodoform.	Gives no iodoform.

Chloral hydrate and alcoholate should be completely volatile. Their aqueous solutions should be perfectly neutral to litmus.

411. An aqueous solution of chloral hydrate gives no reaction with silver nitrate in the cold, but when the liquid is heated to boiling, and a few drops of ammonia added, a metallic mirror is readily produced. If kept some time, chloral hydrate contains a trace of hydrochloric acid, and the solution in water then gives a cloud with nitrate of silver; the production of a distinct precipitate indicates serious impurity.

412. When the water of hydration is in excess, chloral hydrate is deliquescent, and in warm weather even melts. Hence it is now

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[1] Other impurities besides the alcoholate cause a darkening with sulphuric acid.

generally made slightly deficient in hydration. If more than a shade short of being fully hydrated the product has a tendency to become acid, and ultimately partially insoluble from formation of metachloral.

413. The solidifying point of melted chloral hydrate is an indication of some value. The sample should be placed in a small test-tube, fused, and the tube immersed in water at about 55° C. A thermometer is placed in the chloral, and the temperature at which the liquid becomes opalescent noted. The best chloral hydrate solidifies at about 48° to 49° C., and the best *practically* adjusted specimens within half a degree of 50° C. A low freezing point indicates excess of water, and such specimens are liable to deliquesce. Small granular crystals and saccharoid masses are purer than large crystals or needles.

414. The boiling point of chloral hydrate is also of service as a test of purity. The sample should be placed in a test-tube with some broken glass. With a pure sample, rapid boiling will commence at 97° C., and the temperature will not vary very much till fully one-half has been volatilised. Chloral hydrate appears, however, to undergo slow decomposition at its boiling point, so that the first portions of the distillate are under-hydrated, and the last over-hydrated. The boiling point consequently undergoes a gradual rise. The best commercial specimens, *i.e.*, those slightly under-hydrated, begin to boil throughout the liquid at about 96°·5 C. The under-hydrated portion boils off in a few seconds, and the boiling point rises to 97° C., and finally to 97°·5 or 98° C., by the time half the liquid has boiled off. A boiling point above 98° C. indicates an over-hydrated and deliquescent sample. If the boiling fairly commences below 95° C., the sample is too much under-hydrated, and is liable to decompose on keeping.

415. Detection and Determination of Chloral.

Valuable as chloral hydrate is as a sedative and hypnotic, fatal poisoning by it is not uncommon. In such cases it may be detected by the same means as chloroform (par. 425), into which it appears to be converted in the system.

Solutions of chloral reduce Fehling's solution on heating. The reaction may be employed to detect traces of chloral if other reducing substances be absent, and might probably be made quantitative.

Traces of chloral may be detected by Hofmann's delicate test for chloroform (see par. 425, *a*); also, by boiling the liquid and passing the vapour through a red-hot tube, when hydrochloric acid will be formed, and hence the condensed water will precipitate silver nitrate.

416. *a.* For the determination of real *chloral* in commercial samples of the hydrate advantage may be taken of its reaction with alkalies, which results in the separation of chloroform and the production of an alkaline formate:—

$$C_2HCl_3O,H_2O + NaHO = NaCHO_2 + H_2O + CHCl_3.$$

K. Müller places 25 grammes of the sample in a finely-graduated tube, and then adds a strong solution of caustic potash, in quantity rather more than sufficient for the above reaction. A large excess of alkali must be avoided. The tube must be kept well cooled, as the action is very violent at first. Afterwards, the tube may be closed and the mixture shaken. After resting an hour or two the liquid becomes clear, and separates into two layers. The lower layer is chloroform, and, after being brought to a temperature of 17° C., the volume may be read off. Its density is 1·491, and hence the measure of chloroform in c.c., multiplied by 1·84, gives the grammes of anhydrous chloral in the quantity of the sample employed. If the factor 2·064 be substituted, the product will be the weight of chloral hydrate present. Müller obtained by this process an average of 71·6 per cent. of chloroform from pure chloral hydrate, against 72·2 per cent. as required by theory.

b. C. H. Wood (*Pharm. Jour.* [3] i. 703) distils the sample of chloral hydrate with milk of lime. 10 grammes weight of the sample is dissolved in 50 c.c. of water contained in a small flask, and 4 grammes of slaked lime is added. A cork with a tube bent twice at right angles is adapted to the flask, the outer end of the tube being somewhat drawn out and immersed in a small quantity of water, contained in a narrow graduated glass tube surrounded with cold water. A gentle heat is applied to the flask, and the chloroform slowly distilled over. After a few minutes the heat is gradually increased, so as to keep the mixture boiling, the operation being continued till 10 c.c. measure has passed over. Nothing remains but to bring the chloroform to the proper temperature and read off the volume. The addition of a few drops of potash solution destroys the meniscus of the chloroform, and enables the operator to observe the measure accurately. The process does not occupy more than a quarter of an hour. Too much lime occasions frothing, but an excess appears to have no decomposing action on the chloroform. Lieben's iodoform test for alcoholate is readily applied to the aqueous portion of the distillate. The writer has found this plan convenient and fairly accurate. A correction may advantageously be made for the slight solubility of chloroform. This is about 0·3 c.c. for every 100 c.c. of aqueous liquid.

c. A very simple and accurate modification of the above process for assaying chloral hydrate has been suggested by M. Meyer, and has given the writer very satisfactory results. It has the advantage of being applicable to very moderate quantities of material. 1 or 2 grammes of the sample should be dissolved in water, and any free acid which may be present removed by shaking the liquid with chalk or barium carbonate and subsequently filtering. The filtrate is then treated with a moderate excess of normal caustic soda, and titrated back with acid in the usual way, litmus being used as an indicator. Each c.c. of normal alkali neutralised by the sample corresponds to ·1475 gramme of real chloral (C_2HCl_3O), or ·1655 gramme of chloral hydrate.

Other processes of assaying chloral hydrate have been based on its decomposition by ammonia and on its conversion into anhydrous chloral by sulphuric acid, but they are more liable to error, and are in no way superior to the methods already described.

417. TRICHLOR-ACETIC ACID, $HC_2Cl_3O_2$, is a product of the action of oxidising agents on chloral. When equivalent quantities of chloral hydrate and potassium permanganate are cautiously mixed in concentrated solution, potassium trichloracetate is formed, and may be obtained in white silky crystals by filtering and evaporating the liquid. By the action of alkalies, trichlor-acetic acid yields chloroform and a carbonate, and responds to all other tests for chloral dependent on its conversion into chloroform.

418. **Butyric Chloral. Butyl Chloral.** Butyric trichlor-aldehyde. *Erroneously,* Croton chloral. $C_4H_5Cl_3O = C_3H_4Cl_3.COH$. When chlorine is passed into aldehyde, this substance is formed in addition to ordinary chloral. It bears the same relation to butyl alcohol and butyric acid that ordinary chloral bears to ethyl alcohol and acetic acid.

Butyl chloral was at first called croton chloral, the hydrogen being under-estimated, which led to the supposition that it was the trichlorinated aldehyde of crotonic acid, $C_4H_6O_2$, the fourth member of the acrylic or oleic acid series.

Butyric chloral is a dense oily liquid of peculiar odour, boiling at about 163° C. When treated with a considerable excess of warm water it dissolves, and on cooling deposits

Butyric or **Butyl Chloral Hydrate.** $C_4H_5Cl_3O,H_2O$.

419. This substance forms white silvery crystalline scales melting at 78° C., and having a sweetish melon flavour. The specific gravity is 1·695, that of solid chloral hydrate being 1·818. Butyric chloral hydrate is but little soluble in cold water, but more so in hot. Its solubility is increased by addition of glycerin. It is very soluble in alcohol and ether, but insoluble, or nearly so, in chloro-

form. This last property may be employed to separate it approximately from ordinary chloral hydrate. It differs also from the latter body in its melting and boiling point. The two bodies may also be separated by distillation, ordinary chloral hydrate passing over a little below 100°, while butyric chloral hydrate is decomposed into water, which distils at about 100°, and anhydrous butyric chloral boiling at about 163° C.

When acted on by alkalies, butyric chloral hydrate is at first decomposed with production of a formate and propylic chloroform, $C_3H_5Cl_3$, but this again splits up with formation of a chloride of alkali-metal and dichloride of allylene, $C_3H_4Cl_2$. It is to the production of the last substance that the curious and valuable medicinal effects of butyl chloral are chiefly due.

420. DICHLORIDE OF ALLYLENE is very unstable, being gradually decomposed, even at ordinary temperatures, and acquiring an acid reaction and disagreeable odour. The proneness to change, so marked in some samples of commercial chloroform, and the readiness with which the latter decomposes and becomes acid, are properties not improbably due to the presence of dichloride of allylene. Its presence is probably due to the existence of aldehyde in the crude alcohol used for the preparation of the chloroform. By the action of chlorine the aldehyde is converted into butyl chloral, and this, by subsequent contact with the chalk used for neutralisation, gives dichloride of allylene.

421. CHLOROFORM.

Trichloro-methane. Methenyl trichloride. $CHCl_3$.

Chloroform is generally manufactured by distilling dilute alcohol with hypochlorite and hydrate of calcium (bleaching powder and slaked lime). A complicated reaction ensues,[1] and the product requires careful purification for the removal of secondary products. Chloroform is also prepared by distilling chloral hydrate with dilute alkali, when the following reaction occurs:—

$$\underset{\text{Chloral hydrate.}}{C_2HCl_3O,H_2O} + NaHO = \underset{\text{Sodium formate.}}{NaCHO_2} + H_2O + \underset{\text{Chloroform.}}{CHCl_3}.$$

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[1] The production of chloroform by the action of bleaching powder on alcohol may be represented by the equation :—$4C_2H_6O + 16CaCl_2O = 2CHCl_3 + 3Ca(CHO_2)_2 + 13CaCl_2 + 8H_2O$. Recent researches, however, have shown that the reactions which occur in practice are far more complicated (see note on page 170). It is probably on this account that pure methyl alcohol yields no chloroform on treatment with chlorine and an alkali. Acetone, on the other hand, may be substituted for alcohol in the preparation of chloroform.

The product is purified by treatment with strong sulphuric acid or an alkaline solution of potassium permanganate.

It is extremely probable that the dangerous and fatal effects occasionally attending the administration of chloroform are due to impurities in the commercial article. Hence, the careful preparation and thorough purification of chloroform are of great importance.

422. Chloroform is a colourless limpid liquid, of peculiar odour, and sweet but somewhat burning taste. The anæsthetic effects produced by inhaling its vapour are well known. Pure chloroform is not combustible, but when mixed with alcohol it burns with a smoky flame edged with green.

423. The density is 1·500 at 15° C. and the boiling point 60°·8. According to Thorpe, the reduced and corrected boiling point of chloroform is 61°·2, and the density at 0° C. 1·5266, compared with water at the same temperature.

424. Chloroform is almost insoluble in water (·44 grammes in 100 c.c.), to which, however, it imparts a sweet taste. It is miscible in all proportions with absolute alcohol, ether, benzene, and petroleum spirit. It is soluble to a limited extent in aqueous alcohol.

Chloroform possesses remarkable solvent properties, dissolving many organic bases, fats, wax, resins, camphor, india-rubber, gutta-percha, pitch, iodine, bromine, and phosphorus.

Many important properties of chloroform are described on page 179, *et seq.*

425. DETECTION AND DETERMINATION OF CHLOROFORM.

As a rule, the detection of chloroform itself is less important than the recognition and estimation of other substances in presence of chloroform.

a. A very delicate method for the detection of chloroform in presence of large quantities of alcohol has been described by A. W. Hofmann. All that is necessary is to add some alcoholic soda and a little aniline to the liquid to be tested. Either immediately or on gently warming the mixture, a strong and peculiar smell will be observed, due to the formation of benzo-isonitrile (phenyl isocyanide), C_7H_5N. Bromoform and iodoform give the same reaction, as also do chloral, trichlor-acetic acid, and all other bodies which yield either of the above products by treatment with alkalies. On the other hand, ethylidene chloride, $C_2H_4Cl_2$, gives no isonitrile under the same conditions. The test is so delicate that one part of chloroform dissolved in 5000 parts of alcohol may be detected with certainty by means of it.

b. The reduction of Fehling's alkaline copper solution is also a

good and delicate test for chloroform, with which it reacts thus:—
$CHCl_3 + 5KHO + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O$.

When the solution is heated, the formation of the yellow-red cuprous oxide occurs very promptly. The reaction might probably be used for the determination of chloroform in the absence of other reducing agents, especially if the test were applied to a liquid obtained by distillation. Chlor-ethylidene and alcohol do not interfere with the test.

c. When chloroform vapour mixed with hydrogen is passed through a red-hot tube, it is decomposed with production of hydrochloric acid. This fact may be employed for the detection and estimation of chloroform. The sample should be boiled in a small flask through which a current of hydrogen is allowed to pass. The mixed hydrogen and chloroform vapour are then caused to traverse a short length of heated combustion tube containing platinum wire-gauze.

The products of the reaction are collected in a bulb-tube containing water, and the hydrochloric acid produced is titrated with standard alkali, or precipitated with nitrate of silver. 109·5 parts of hydrochloric acid, or 430·5 of chloride of silver, represent 119·5 of chloroform. Berthelot points out that the reaction with silver is apt to be vitiated by the presence of acetylene and hydrocyanic acid, and recommends that the aqueous solution of the gases should be well boiled before adding silver nitrate.

This process is especially useful for the determination of small quantities of chloroform contained in other non-chlorinated liquids. It may be employed for the detection and estimation of chloroform in blood. When its detection only is required, a current of air may be substituted for the hydrogen. There is no occasion to heat the blood.

d. Vitali suggests that the mixture of hydrogen with chloroform vapour obtained as in the last reaction should be submitted to Hofmann's isonitrile reaction (test *a*), or passed through a freshly prepared mixture of thymol and solid caustic potassa, when if chloroform be present the mixture will be coloured a fine reddish-violet.

e. When chloroform is added to a solution of α- or β- naphthol in strong caustic potash, and the liquid is heated to about 50° C., a fine Prussian blue colour is developed, changing in contact with the air to blue-green, green, green-brown, and finally brown.

Chloral and chloral hydrate resemble chloroform in their behaviour with naphthol.

426. Commercial Chloroform.

Many specimens of commercial chloroform undergo more or less change on keeping. According to Personne, samples liable to alteration always contain chloro-carbonic ether, $C_2H_5CO_2Cl$. The change has also been attributed to the presence of dichloride of allylene. At any rate, certain specimens of chloroform, originally of good quality, on keeping become impregnated with hydrochloric, hypochlorous, and formic acids. J. Regnauld has found that carbon oxychloride, $COCl_2$, was readily produced by the action of ozonised air on chloroform, and considers the accidental presence of this body in chloroform very common. He has also found that very carefully prepared chloroform can be kept unchanged if exposed to air or light simply, but that the combined action of air and light rapidly affects the purity of the preparation. The change is entirely prevented by the addition of 0·1 per cent. of alcohol, which is said to be more efficacious than a larger proportion.

In addition to the impurities resultant from decomposition by keeping, commercial chloroform may contain alcohol, aldehyde, and various chlorinated oils. These last are very injurious and even poisonous, and are detected and eliminated with considerable difficulty. Other products may be present if the alcohol employed for the manufacture of the chloroform contained methyl or amyl compounds. Methylic alcohol is generally supposed to be capable of forming chloroform, but, from experiments on the perfectly pure substance, this notion seems to have been disproved. Alcohol and aldehyde are sometimes added to chloroform in very considerable proportions. The adulteration of chloroform with ether and acetic ether has also been practised.

427. *Free chlorine* and *hypochlorous* and *hydrochloric acids* in chloroform may be recognised by shaking the sample with a solution of nitrate of silver, which in presence of either of the above impurities will produce a white precipitate, whereas chloroform itself gives no reaction with silver nitrate, either in aqueous or alcoholic solution. If the precipitate blacken on heating the presence of *aldehyde* or *formic acid* is indicated. Free chlorine and hypochlorous acid are distinguished from hydrochloric acid by their power of bleaching instead of merely reddening litmus, and by liberating iodine from a solution of pure iodide of potassium when the sample is shaken with it. The liberated iodine colours the chloroform reddish-violet.

428. *Dichloride of Ethylene*, $C_2H_4Cl_2$, may be detected in chloroform by drying the sample by agitation with dry carbonate of potassium, and then adding metallic potassium. This does not act on pure chloroform, but in presence of the above impurity

it produces chlor-ethylene, C_2H_3Cl, a gas of an alliaceous odour. It is very doubtful whether the substance in chloroform of the formula $C_2H_4Cl_2$ is always dichloride of ethylene. It is probably more frequently the isomer ethylidene chloride, $CH_3.CHCl_2$ (see par. 346).

429. The presence of *ethyl chloride*, C_2H_5Cl, in chloroform is best recognised by distilling the sample with water in a water-bath. The first portions of the distillate will have a distinct smell of the foreign body.

430. "METHYLATED CHLOROFORM" is chloroform prepared from wood spirit, or methylated spirit. It is a mistake to suppose that methylated chloroform has received an actual addition of wood spirit, but such chloroform is liable to be much less pure than that obtained solely from ethylic alcohol. Chloroform prepared from methylated spirit is more difficult to purify than that made from pure alcohol, but a product is now manufactured from the former source which appears to be equal in all respects to the dearer article.

Imperfectly purified methylated chloroform is specifically lighter than the pure substance, has an empyreumatic odour, and produces disagreeable sensations when inhaled. In some cases such chloroform seems actually poisonous, and produces general and rapid prostration. Such impure chloroform contains several units per cent. of a *chlorinated oil*, lighter than water and boiling at a much higher temperature than chloroform. A similar but different oil (heavier than water) is sometimes contained in much smaller quantity in chloroform prepared from alcohol containing no methyl compounds.

431. Chloroform is not soluble in strong sulphuric acid, and, when pure, is not acted on until after the lapse of some time, when shaken with that reagent. Any darkening of the acid which occurs may be due to the presence of *aldehyde*, *wood spirit*, chlorinated oils, &c. Pure chloroform floats on strong sulphuric acid with a contact-surface convex downwards, but if impure gives a plane contact-surface.

432. The boiling point of chloroform is a valuable indication of its purity. Pure chloroform boils at 60°·8 C. The presence of ½ per cent. of alcohol reduces the boiling point to 59°·8 or 60° C. A boiling point higher than 61° C. indicates the presence of *amyl* or *butyl compounds*. In some cases the boiling point of the last portions distilled is as high at 70° C.

Pure chloroform volatilises entirely without disagreeable smell. The impurities are generally less volatile. Many kinds of impurity in chloroform may be readily recognised by the disagreeable odour left on the evaporation of the sample from a cloth or filter-paper soaked with it.

433. Pure chloroform is not *visibly* altered when heated with solution of potassa, though it is slowly acted on with formation of a formate and chloride of the alkali metal. In alcoholic solution this reaction occurs rapidly. In presence of *aldehyde* or *acetone* the solution of potassa becomes coloured brown.

434. Any considerable admixture of *ether* with chloroform would be indicated by the inflammability and diminished density of the liquid.

435. Perfectly pure chloroform does not change the colour of an alkaline solution of permanganate of potassium from violet to green within half a minute, but as the change is caused by alcohol equally with more objectionable impurities, the reaction has little practical value.

436. The most delicate test for the presence of *alcohol* in chloroform is that of A. Lieben, as modified by Hager. The sample should be agitated with five measures of water, the liquid passed through a wet filter, and the filtrate examined as described in par. 151, *c*.

437. Caustic potash is quite insoluble in dry chloroform, but dissolves sensibly in presence of *water* or *alcohol*. If, therefore, a piece of stick potash be fused on a loop of platinum wire, and introduced into some of the chloroform contained in a dry test-tube, the liquid will not acquire the power of turning red litmus paper blue, unless water or alcohol be present. If more than a trace of alcohol be present, the decanted chloroform, when shaken with water, yields a liquid which gives a blue precipitate with a solution of sulphate of copper. To use this test with certainty to distinguish between water and alcohol, the sample must be first shaken with recently-ignited potassium carbonate. This treatment will remove water but not alcohol, so that if the chloroform still possesses the power of dissolving caustic potash alcohol must be present.

438. Oudemanns (*Zeitsch. Anal. Chem.*, xi. 409) determines the proportion of alcohol contained in commercial chloroform by shaking 10 c.c. of the sample in a flask with an excess of pure dry cinchonine. The flask is kept for an hour at a temperature of 17° C., with frequent agitation. The liquid is then passed through a dry filter, and 5 c.c. of the filtrate evaporated to dryness in a small hand beaker. The following are the number of milligrammes of residual alkaloid yielded by 5 c.c. of chloroform containing various proportions of alcohol:—

Residue.	Alcohol.	Residue.	Alcohol.
Milligrammes.	Per cent.	Milligrammes.	Per cent.
21	0	260	6
67	1	290	7
111	2	318	8
152	3	343	9
190	4	346	10
226	5		

439. Stoedeler has suggested fuchsine for detecting alcohol in chloroform. The sample becomes coloured red if alcohol be present, the depth of colour varying with the proportion of alcohol. The author found (*Analyst*, ii. 97) that, even after agitation with chloride of calcium, the chloroform became coloured on adding fuchsine, but by agitating the sample with one-fifth of its bulk of strong sulphuric acid, and subsequently removing traces of the latter by shaking with dry precipitated carbonate of barium, the chloroform was obtained so pure as to give only a very slight coloration with fuchsine. This purified chloroform could then be used in a similar manner to the ether in par. 282, for determining small proportions of alcohol in chloroform. Chloroform may also be purified from water, alcohol, and ether by agitating with sulphuric acid as above, separating the acid, shaking the chloroform with a strong solution of sodium carbonate, and, lastly, distilling it over freshly burnt lime.

440. When the quantity of alcohol in chloroform exceeds 1 or 2 per cent., the proportion may be determined with tolerable accuracy by shaking 20 c.c. of the sample in a graduated tube with 80 c.c. of water. If the chloroform be pure it will sink to the bottom in clear globules, but in the presence of alcohol the liquid and the surface of the drops will become dim and opalescent. The reduction in the volume of the chloroform shows the proportion of alcohol in the amount taken. The addition of a few drops of solution of potassa destroys the meniscus, and enables the volume to be read more accurately. The aqueous liquid may be tested for sulphuric acid by barium chloride; for free chlorine or hypochlorous acid by starch and iodide of potassium; for hydrochloric acid by silver nitrate; and the presence of alcohol definitely proved by the iodoform test.

441. The proportion of *alcohol* present in chloroform can in some cases be ascertained from the density. According to C. Remys (*Archiv. der Pharm.*, [3] v. 31) pure chloroform has a density of 1·500 at 15° C., the presence of ⅛ per cent. of alcohol reducing the density by ·002, and ½ per cent. by ·008. According

to A. H. Mason, chloroform containing 1 per cent. of alcohol has a density of 1·497 at 15°·5 C. The chloroform of the British Pharmacopœia has a density of 1·49. Chloroform containing amyl or butyl compounds has a higher density than 1·500.

442. SPIRIT OF CHLOROFORM, B.P., is a solution of chloroform in 19 measures of rectified spirit (55° O.P.) and should have a density of ·871. A lower specific gravity may be due to deficiency of chloroform or to the use of spirit of 60° O.P. "Chloric Ether" is a spirituous solution of chloroform of very varying strength.

The proportion of chloroform present in spirit of chloroform, "chloric ether," and similar preparations, may be ascertained with accuracy by introducing into a narrow graduated tube 20 c.c. of the sample and 30 c.c. of dilute sulphuric acid (1 to 6) coloured with a little fuchsine. A cork is then inserted and the contents of the tube thoroughly shaken. When the chloroform has separated, the tube is tapped to cause any floating globules to sink, and about 10 c.c. of petroleum spirit is cautiously poured on the surface of the acid. The cork is reinserted, and the volume of petroleum spirit employed is carefully noted, when the contents of the tube are well mixed by agitation. After separation the volume of petroleum spirit is again observed, when its increase will be due to the dissolved chloroform. Better results are obtainable in this way than without petroleum spirit, but great care is necessary to avoid error from expansion or contraction through alteration of temperature. Hence, before observing the volume of petroleum spirit originally used, and again before the final reading, the tube should be immersed in a cylinder of cold water for a short time. The process gives inaccurate results when the proportion of chloroform exceeds about 30 per cent. In such cases the method in par. 440 should be employed.

The chloroform in mixtures of chloroform and alcohol may also be determined by decomposition with alkali in the manner described in par. 293.

443. **Methylene Dichloride.** Bichloride of Methylene. CH_2Cl_2.

This substance is the second member of the series of products arising from the action of chlorine on marsh gas, as shown in the annexed table.

444. Methylene dichloride is obtained by exposing the vapour of methyl chloride in admixture with chlorine to the action of daylight, in a large glass globe. The products are passed through two Woulffe's bottles, and then into a flask surrounded by a freezing mixture. The former chiefly retain chloroform, while the

methylene dichloride condenses in the flask. It may also be obtained by the reduction of chloroform in alcoholic solution by zinc and hydrochloric acid.

Formula.	Name.	Boiling Point. ° C.	Specific Gravity.
CH_4	Methane ; marsh gas, ...	...	...
CH_3Cl	Chlormethane ; methyl chloride, .	-23	·999 at - 30° ·952 at 0°
CH_2Cl_2	Dichlormethane ; methylene dichlóride,	41·6	1·36 at 0°
$CHCl_3$	Trichlormethane ; chloroform, . .	61·	1·500 at 15° 1·526 at 0°
CCl_4	Tetrachlormethane ; carbon tetrachloride, ...	78·	1·630 at 0° 1·599 at 15°

445. Bichloride of methylene is a powerful anæsthetic, but is said to have a depressing effect. Being more expensive than chloroform, the latter liquid is sometimes substituted and sold for the former, which it closely resembles in odour. The two bodies may be distinguished by their specific gravity and boiling points. The dichlormethane burns with a smoky flame and dissolves iodine with brown colour, while chloroform unmixed with alcohol burns with great difficulty, giving a green-edged flame, and dissolves iodine with reddish-violet colour.

446. A mixture of alcohol and chloroform has been substituted for methylene dichloride. On shaking the sample with water, the alcohol would be dissolved, and the chloroform would then be recognisable by its density.

447. **Bromoform,** $CHBr_3$.

This body closely resembles chloroform, but boils at 150° to 152° C. Its density is 2·9 at 12° C., or, according to E. Schmidt, 2·775 at 14°·5 C. It solidifies at − 9° C.

Caustic potash converts bromoform into chloride and formate of potassium. By the action of alcoholic potash, gas is evolved, consisting of one volume of carbon monoxide and three of ethylene; thus :—$CHBr_3 + 3KC_2H_5O = 3KBr + 2H_2O + CO + 3C_2H_4$

448. Bromoform is not unfrequently present in commercial bromine, even to the extent of 10 per cent. It may be detected by fractional distillation of the bromine on the water-bath, or by treating the sample with excess of solution of potassium iodide, and then adding sufficient sodium thiosulphate (hyposulphite) to take up the iodine set free. The characteristic odour of bromoform then becomes apparent.

449. **Iodoform,** CHI_3.

Iodoform is produced in Lieben's test for alcohol (par. 151, *c.*). It may be conveniently prepared by heating 1 part of iodine, 1 of alcohol, 2 of crystallised sodium carbonate, and 10 of water to about 70 to 80° C., till decolorised, when the iodoform separates as lemon-yellow powder, which may be filtered from the liquid, washed with cold water, and dried.

450. Iodoform is a light yellow, shining, crystalline solid, having a persistent odour resembling saffron, or a solution of iodine in chloroform. It has a density of 2·0, sublimes at a gentle heat without change, distils with vapour of water, and volatilises sensibly at ordinary temperatures. Heated strongly, it is decomposed with formation of violet vapours of iodine, and deposition of carbon.

Iodoform is nearly insoluble in water (1 part in 13,000) and dilute alkaline and acid liquids; sparingly soluble in rectified spirit (1 in 80), but more readily in absolute alcohol (1 in 25); and with facility in ether, chloroform, and carbon disulphide. It is also dissolved by many essential oils, and sparingly by glycerin, benzene, and petroleum spirit.

Iodoform is employed in medicine as an antiseptic dressing and for other purposes.

451. In its chemical reactions iodoform closely resembles chloroform. Its microscopic appearance is very characteristic, its usual forms being hexagonal plates, stars, and rosettes.

Iodoform may be extracted from urine and other aqueous liquids by agitation with ether. On allowing the ethereal layer to evaporate spontaneously, the iodoform may sometimes be recognised by examining the residue under the microscope. If no distinct forms are observable, the residue should be taken up with a little absolute alcohol, and three or four drops of the clear solution added to a minute quantity of a solution of phenol in caustic soda. The mixture is cautiously heated, when a red deposit will be formed at the bottom of the tube, soluble in dilute alcohol with crimson colour (Lustgarten, *Jour. Chem. Soc.*, xliv. 243).

452. COMMERCIAL IODOFORM.

On agitation with water, iodoform should not yield a liquid precipitable, after filtration, by barium chloride or silver nitrate. It should leave no soluble residue on ignition in the air; and should be wholly soluble in boiling alcohol, but insoluble in brine.

453. *Picric acid* has been used as an adulterant of iodoform (*Pharm. Jour.*, [3] xiv. 493). It may be detected by agitating the sample with dilute solution of caustic soda or carbonate of sodium, carefully neutralising the filtrate with acetic acid, and adding potassium nitrate, when a yellow precipitate of the spar-

ingly soluble potassium picrate will be thrown down. The iodoform may also be separated by treating the sample with caustic soda solution and agitating the liquid with chloroform, when only the picric acid will remain in the aqueous liquid. Picric acid may also be detected by the reddish-brown coloration produced on heating the cold aqueous solution of the sample with potassium cyanide.

SUGARS.

UNDER the generic name of sugars are included a large number of bodies occurring naturally in the animal or vegetable kingdoms, or produced from the so-called *glucosides* by the action of ferments or dilute acids.

The sugars constitute a group of closely-allied bodies, in many cases distinguishable from each other only with considerable difficulty, while their quantitative separation is frequently impossible in the present condition of chemistry.

As a class, the sugars are crystallisable, readily soluble in water, somewhat less soluble or wholly insoluble in alcohol, and insoluble in ether and other solvents immiscible with water.

A *sweet taste* is possessed by nearly all sugars, to a greater or less extent, though in some of the rarer saccharoids the character is very feebly marked. Glycerin and glycol have a sweet taste, and, like the sugars, are polyatomic aclohols, but the same analogy of constitution does not extend to glycocine (the so-called "sugar of gelatin"), or to the sweet salts of lead and yttrium.

In many cases the sugars exert a powerful rotatory action on a ray of polarised light, the direction and extent of the rotation being peculiar to each sugar. Hence the *optical activity* is a valuable means of estimating and differentiating sugars, and is fully discussed in a special section (par. 454 *et seq.*).

CONSTITUTION AND CLASSIFICATION OF SUGARS.

Most of the sugars have the constitution of hexatomic alcohols, or of aldehydes or ethers derived therefrom. Thus mannite, which is a-hexone alcohol, $C_6H_8(OH)_6$, by limited oxidation with platinum-black yields the corresponding aldehyde, $C_6H_6(OH)_6$, which is a true sugar called mannitose. Conversely, by the action of nascent hydrogen, the aldehyde mannitose can be again reduced to mannite. Mannite also results from the reduction of dextrose and lævulose, which are sugars isomeric with mannitol; while the action of nascent hydrogen on another isomer, galactose, results in the production of dulcite, or β-hexone alcohol, isomeric with mannite.

The saturated alcohols of which mannite, $C_6H_{14}O_6$, is the type, form the class of sugars called *saccharoids*. Their characters are detailed more fully in the table on page 189.

The aldehydes of the bodies of the last group constitute the important class of sugars called *glucoses*, $C_6H_{12}O_6$. These have themselves, to some extent, the characters of alcohols.

The oxygen-ethers or first anhydrides of the glucoses constitute the class of sugars called *saccharoses*, $C_{12}H_{22}O_{11}$, of which cane sugar is the type. The conversion of saccharoses into glucoses by hydrolysis is readily effected, but the reverse change has not been realised (unless very recently).

By the action of heat on the glucoses and saccharoses the elements of water are eliminated, and other anhydrides result. Thus dextrose, $C_6H_{12}O_6$, yields glucosan, $C_6H_{10}O_5$.

The following tables show the distinguishing chemical and physical characters of the principal sugars, which are arranged in the three classes of *saccharoids*, *glucoses*, *and saccharoses*.

In order to abridge the descriptions as much as possible, initial letters are used in the tables, the characters given after them referring to the properties or reactions of the sugars when examined or treated in the respective manners indicated below :—

(*a*) Specific gravity of the sugar.

(*b*) Character of the crystals and general appearance of the sugar.

(*c*) Action of heat on the sugar.

(*d*) Solubility of the sugar in water, and taste of the solution.

(*e*) Solubility of the sugar in alcohol.

(*f*) Products of the action of moderately concentrated nitric acid on the sugar.

(*g*) Reaction of the sugar with concentrated sulphuric acid.

(*h*) Products formed by boiling the sugar with diluted sulphuric acid.

(*i*) Effect of yeast on the aqueous solution of the sugar.

(*j*) Products of the action of cheese and chalk on the aqueous solution of the sugar.

(*k*) Reaction of the sugar with strong solution of caustic alkali.

(*l*) Effect on Fehling's copper solution, when heated to 100° C. with an aqueous solution of the sugar.

(*m*) Reaction of the sugar on ammonio-nitrate of silver at 100° C.

(*n*) Reaction of the aqueous solution of the sugar with ammoniacal acetate of lead.

1. SACCHAROIDS, or NON-FERMENTABLE SUGARS.—This group includes the hexatomic alcohols mannite, dulcite, and sorbite, $C_6H_{14}O_6 = C_6H_8(OH)_6$; and some unimportant bodies of the same formula, or differing therefrom by the elements of water. They are not capable of undergoing fermentation either with yeast or with cheese and chalk.

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Mannite, Mannitol, or α-Hexone alcohol.	Manna; celery; algæ; reduction of glucose.	$C_6H_{14}O_6$ $= C_6H_8(OH)_6$	0[1]	(*b*) Anhydrous, four-sided trimetric prisms. (*c*) Fuses at 166°; at about 200° forms mannitan, as a slightly sweet deliquescent syrup. (*d*) Soluble in 6½ parts, cold; solution slightly sweet. (*e*) Soluble, very slightly so in absolute alcohol. (*f*) Saccharic and oxalic acids. (*g*) Sulphomannitic acid. (*h*) Unaffected. (*i*) and (*j*) Not fermentable, or only very slowly. (*k*) Not coloured. (*l*) Not reduced. (*m*) Reduced. (See "Honey.")
Dulcite, or Dulcitol, or β-Hexone alcohol.	*Melampyrum nemorosum*; action of nascent hydrogen on galactose.	$C_6H_{14}O_6$ $= C_6H_8(OH)_6$	0	(*b*) Anhydrous warty masses or hard monoclinic prisms. (*c*) Fuses at 188°. Prolonged heating at 200° forms dulcitan as a viscous syrup. (*d*) Cold, 3·7 per cent. (*e*) Very slightly soluble. (*f*) Mucic acid (*not* saccharic acid). (*g*) Not carbonised. (*i*) and (*j*) Not fermentable. (*k*) Not affected. (*l*) Not reduced. (*n*) Not precipitated.
Hesperidin sugar.	...	$C_6H_{14}O_6$	...	(*a*) Monoclinic. (*b*) Melts at 70° to 76°. (*e*) Sparingly soluble in hot absolute alcohol, more easily in dilute. (*l*) Not reduced. Dextro-rotatory.
Persite, or Persitol.	*Laurus persea.*	$C_6H_{14}O_6$	0	(*c*) Fuses at 184° and loses water at 250°. (*d*) Cold, 17 parts, hot, readily soluble, separating as farinaceous mass on cooling. (*e*) Soluble in hot alcohol, deposited in slender needles on cooling. (*p*) Oxalic acid (*not* mucic acid). (*i*) and (*j*) Not fermentable. (*l*) Not reduced.
Iso-dulcite.	Action of dilute acids on quercitrin.	$C_6H_{14}O_6$, or $C_6H_{12}O_5 + Aq.$	Sj = +8·4	*b*) Crystals resemble cane sugar. (*c*) Melts at 92° and loses water between 105° and 110°. (*d*) 50 per cent. in the cold; solution sweet. (*e*) Soluble. (*g*) Turns brown. (*i*) and (*j*) Not fermentable. (*k*) Turns brown. (*l*) Reduced.
orbite.	Berries of mountain ash.	$C_6H_{14}O_6 + \frac{1}{2} Aq.$	0	(*c*) Becomes anhydrous; melts at 110°. (*g*) Not carbonised. (*i*) and (*j*) Not fermentable. (*k*) No coloration; distinction from sorbin. (*l*) Not reduced.
Raffinose.	Beet-root.	$C_6H_{14}O_7$	S = 117°·3	
Quercite, or Quercitol.	Acorns.	$C_6H_{12}O_5$	S = +33·5	(*b*) Transparent monoclinic prisms. (*c*) Fuses at 235°. (*d*) and (*e*) Soluble. (*f*) Oxalic acid. (*g*) Not coloured. (*i*) and (*j*) Not fermentable. (*k*) Not coloured. (*l*) Not reduced.
Pinite.	*Pinus Lambertiana.*	$C_6H_{12}O_5$	Sj = +58·6	(*a*) 1·52. (*b*) Radiated crystalline nodules. (*d*) Very soluble; solution very sweet. (*e*) Sparingly soluble. (*f*) Mucic acid. (*i*) and (*j*) Not fermentable. (*l*) Not reduced. (*n*) Precipitated.
Erythro-mannite.	Lichens.	$C_4H_{10}O_4$	0	(*b*) Pyramidal prisms. (*c*) Fuses at 118°. (*d*) and (*e*) Soluble. (*f*) Forms *no* mucic acid. (*i*) and (*j*) Not fermentable. (*l*) Not reduced. (*n*) Not precipitated.

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[1] According to some authorities, mannite has a very feeble lævo-rotatory power. Addition of borax renders the aqueous solution strongly dextro-rotatory.

II. **Glucoses.**—These sugars usually contain two atoms of hydrogen less than the members of Group I. (saccharoïds), and hence may be regarded as the aldehydes of hexatomic alcohols. In fact, ordinary dextrose, $C_6H_{12}O_6$, may be converted into mannite, $C_6H_{14}O_6$, by the action of nascent hydrogen, just as acetic aldehyde may be reduced to ordinary alcohol by the same means. The first three of the glucoses described in the following table present few chemical differences, but are distinguished by their action on polarised light and some other characters. On oxidation, they yield saccharic acid. Galactose differs from them in yielding mucic acid. The first four glucoses in the table readily undergo the alcoholic fermentation in contact with yeast, and reduce hot Fehling's solution and ammonio-nitrate of silver; but inosite, sorbyn, and eucalyn do not undergo the alcoholic fermentation with yeast, though they yield lactic and butyric acids under the influence of cheese and chalk. The body produced by "inverting" cane sugar is a mixture of equal parts of dextrose and lævulose (see par. 672). Dambose, $C_3H_6O_3$, and its analogues are polyatomic alcohols allied to the glucoses.

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Sucro-dextrose, dextro-glucose, dextrose, grape sugar, starch sugar.	Honey; sweet fruits; diabetic urine; action of dilute acids on starch and glucosides.	$C_6H_{12}O_6+Aq.$	SD = +52·3 Sj = +58·0 (See par. 667.)	(*b*) From aqueous solution, in granular warty masses containing 1 Aq.; crystallises from alcohol in anhydrous microscopic needles. (*c*) Becomes anhydrous below 100° C.; melts at 140°; at 170° yields glucosan, $C_6H_{10}O_5$. (*d*) Cold, 100 per cent., hot in all proportions; solution less sweet than that of cane sugar. (*e*) Soluble. (*f*) Saccharic acid. (*g*) Forms sulpho-saccharic acid without charring. (*h*) Not affected till after long time. (*i*) Easily undergoes vinous fermentation. (*k*) Turns brown. (*l*) 10CuO reduced. (*m*) Reduced. (See par. 664.)
Sucro-lævulose, lævo-glucose, lævulose, mucoid sugar.	Honey, together with sucrose and dextrose; fruits; obtained pure by the action of dilute acids on inulin.	$C_6H_{12}O_6$	SD = −98·4 at 15° C. Sj = −109·2 at 15° C. (See par. 670.)	(*b*) Syrupy liquid, forming with difficulty an anhydrous amorphous solid. (*c*) At about 170° yields lævulosan, $C_6H_{10}O_5$. (*d*) Solution much sweeter than that of dextrose. (*e*) More soluble than dextrose. Lævulose closely resembles dextrose in other characters, but is more easily altered by heat and acids, and offers greater resistance to alkalies and ferments. Its reducing power on Sachsse's solution (see par. 542) is less than that of dextrose. By the action of chlorine, lævulose forms glycolic acid, dextrose giving dextronic acid. (See par. 669.)

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Mannitose.	Oxidation of mannite.	$C_6H_{12}O_6$	0	(*b*) Syrupy. (*e*) Soluble. In all other characters but optical activity, mannitose closely resembles lævulose.
Galactose, lactose.	Action of dilute acids on milk sugar.	$C_6H_{12}O_6$	$S_D=81{\cdot}3$ (See par. 677.)	(*c*) Sparingly soluble in cold alcohol. (*f*) Yields mucic acid. Resembles dextrose in other reactions, but has less powerful reducing action on Fehling's solution. Probably consists of a mixture of two dextro-rotatory glucoses. (See par. 675.)
Arabinose, pectinose.	Action of dilute acid on arabin.	$C_6H_{12}O_6$	Variable.	At least four or five glucoses are produced by the action of dilute acid on arabin, and differ from each other in their specific rotations and cupric oxide reducing powers.
Inosite, inosol, phaseomannite.	Muscle; kidney-beans; cochineal, &c.	$C_6H_{12}O_6+2$ Aq.	0	(*a*) 1·524. (*b*) Cauliflower-like masses, or monoclinic prisms resembling gypsum. (*c*) When rendered anhydrous melts at 210° C. (*d*) Water at 19° C. dissolves 16 per cent. of its weight; solution sweet. (*e*) Insoluble in absolute alcohol, slightly in hot dilute spirit. (*f*) Evaporated nearly to dryness with a little nitric acid, and ammonia and $CaCl_2$ added, and again evaporated gives rose-red colour. (*g*) Not charred even at 100° C. (*i*) Not fermentable. (*j*) Forms lactic, butyric, and carbonic acids. (*g*), (*h*), and (*k*) Not affected even at 100° C. (*l*) Reduced with difficulty.
Scyllite.	Kidney, liver, &c., of cartilaginous fishes.	$C_6H_{12}O_6$	...	(*b*) Anhydrous monoclinic prisms. Slightly sweet. Resembles inosite.
Sorbinose, sorbin.	Ripe mountain-ash berries.	$C_6H_{12}O_6$	$S_j=-46{\cdot}9$	(*b*) Hard trimetric prisms, or rhombic octahedra. (*d*) Easily soluble (200 per cent.); solution very sweet. (*e*) Almost insoluble. (*f*) Tartaric, racemic, oxalic, and aposorbic acids. The last crystallises in rhombic scales, melting at 100°. (*h*) Not affected. (*i*) Not fermentable. (*j*) Lactic and butyric acids, and alcohol. (*k*) Turns yellow or brown. (*l*) Reduced. (*n*) Precipitated. Yields glycolic acid by the action of chlorine.
Eucalyptose, eucalyn.	Action of dilute acids on, or fermentation of, mellitose.	$C_6H_{12}O_6+1$ Aq.	$S_R=+65°$	(*b*) Uncrystallisable syrup, rendered anhydrous at 100° C., only slightly sweet. (*f*) Oxalic acid. (*g*) Chars. (*h*) No action. (*i*) Not fermentable. (*j*) Lactic and butyric acids. Brown colour. (*l*) Reduced.

III. SACCHAROSES.[1] $C_{12}H_{22}O_{11}(=2C_6H_{12}O_6-H_2O)$.—These sugars are related to the glucoses (Group II.) in the same manner as di-ethylenic alcohol is to glycol, or di-glycerin to glycerin (glycerol). They differ chemically from the glucoses by being less powerful reducing agents, and hence having, with the exception of maltose and lactose, little or no action on Fehling's solution; in being charred by sulphuric acid; and in not being capable of *direct* fermentation, though by the action of yeast, or by boiling with dilute acids, they are converted with greater or less facility into glucoses, and then undergo fermentation; the alcohol produced being about 51 to 51·5 per cent. of the weight of the original saccharose employed, against a production of only 48 to 49 per cent from glucoses.

Name.	Origin and Principal Modes of Formation.	Formula.[1]	Sp. Rotatory Power.	Other Characters.
Sucrose, saccharose, cane-sugar.	Sugar-cane; maple; white beet; maize; date-palm.	$C_{12}H_{22}O_{11}$	$S_D=+66^\circ{\cdot}5$ $S_j=+73^\circ{\cdot}8$ (See par. 455.)	(*a*) 1·595. (*b*) Monoclinic prisms, or sparkling crystalline masses. (*c*) Melts at about 160° C., yielding dextrose and lævulosan. (*d*) Cold 200 per cent. hot in all proportions. (*e*) Insoluble in absolute alcohol. (*f*) Oxalic and saccharic acids. (*g*) Chars. (*h*) Forms inverted sugar, a mixture of dextro-and lævo-glucose. (*i*) the same, then alcoholic fermentation. (*k*) Not darkened. (*l*) Not reduced. (*m*) Precipitate of $C_{12}H_{18}Pb_3''O_{11}$. (See par. 554.)
Maltose, malt-sugar.	Malt; together with dextrin, by the limited action of dilute acids or malt-infusion on starch.	$C_{12}H_{22}O_{11}$	$S_D=+139{\cdot}2$ $S_j=+154{\cdot}5$ (See par. 608.)	(*b*) Indefinitely crystalline in hard white crusts or minute needles containing 1 Aq. expelled at 110° C. (*c*) Much less soluble than dextrose. (*d*) Very soluble. (*i*) Yields dextrose, then vinous fermentation. (*l*) About 6 CuO reduced. In general properties closely resembles dextro-glucose. (See par. 606.)
Lactose, lactin, milk-sugar.	Milk of mammals.	$C_{12}H_{22}O_{11}+1$ Aq.	α-variety $S_D=+80^\circ$ β-variety $S_D=+52{\cdot}7^\circ$ (For crystals containing 1 Aq.)	(*a*) 1·525. (*b*) Hard trimetric prisms, or saccharoid masses. containing 1 Aq. (*c*) Becomes anhydrous at about 130° and 180° chars. (*d*) α-form cold, 17 per cent.; β-form, cold, 28 per cent., hot 40 per cent. (*e*) Soluble; insoluble in absolute alcohol. (*f*) Mucic, oxalic, and saccharic acids. (*g*) Charred. (*h*) Yields galactose and dextrose. (*i*) First galactose, then vinous fermentation. (*j*) Lactic acid, alcohol, &c. (*k*) Little affected. (*l*) 7 CuO reduced. (*m*) Reduced. (*n*) Precipitated. (See par. 646.)

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Melitose, eucalypton.	Eucalyptus manna; cotton seed.	$C_{12}H_{22}O_{11}+3$ Aq.	$S_j=+117{\cdot}4$ (For anhydrous substance.)	(*b*) Thin interlaced needles. (*c*) Gives off 2 Aq. at 100° C., and becomes anhydrous at 130°. (*d*) Cold 11 per cent.; hot, easily soluble, solution slightly sweet. (*e*) Insoluble. (*f*) Mucic and much oxalic acid. (*h*) Dextrose and eucalyn, (*i*) Dextrose and eucalyn, the former then fermenting. (*l*) Not reduced. (*n*) Precipitated.
Melezitose.	Larch (*Larix Europæa*); eucalyptus manna.	$C_{12}H_{22}O_{11}$	$S_D=+88°{\cdot}8$ $S_j=+94°{\cdot}8$	(*b*) Small brilliant efflorescent monoclinic prisms containing 1 Aq. (*c*) The anhydrous sugar fuses below 140° without alteration; decomposes at about 200°. (*d*) Easily soluble, solution sweet. (*f*) Oxalic but *no* mucic acid. (*g*) Chars. (*h*) Fermentable glucose. (*i*) Slowly and with difficulty undergoes vinous fermentation. (*k*) Not darkened. (*l*) Not reduced.
Mycose, trehalose.	Ergot; mushrooms; Trehala manna.	$C_{12}H_{22}O_{11}+2$ Aq.	$S_D=+200°$ $S_j=+222°$ (For anhydrous substance.)	(*b*) Shining rhombic prisms, or rectangular octahedra. (*c*) Melts at 100° to 110°, and loses 2 Aq., solidifying again; when anhydrous melts at 210° without decomposition. (*d*) Extremely soluble. (*e*) Soluble in boiling alcohol, almost insoluble in cold. (*f*) Oxalic and saccharic acids, but no mucic acid. (*g*) Colourless in the cold, chars at 100° C. (*h*) Inverted by long boiling, yielding a fermentable glucose. (*i*) Slow and imperfect vinous fermentation. (*k*) Not darkened. (*l*) Not reduced. (*m*) Not precipitated.
Synanthrose.	*Dahlia variabilis*; Jerusalem artichoke.	$C_{12}H_{22}O_{11}$ or perhaps $C_{12}H_{20}O_{10}+$Aq.	0	(*b*) Amorphous, very deliquescent. (*c*) At 140° turns brown, yielding caramel, &c. (*d*) and (*e*) Easily soluble, solutions faintly sweet. (*g*) and (*k*) Not coloured in the cold. (*h*) Dextrose and a lævo-rotatory glucose. The inverted products have a rotatory power of $S_j=-54{\cdot}1°$ at 17°, said to be unaffected by temperature. (*i*) Glucoses, followed by slow vinous fermentation. (*l*) Not reduced. (*n*) Not precipitated.

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[1] It has been recently proposed to use the termination *on* for the sugars of this group, and hence the generic name would be saccharons, and mycon, lacton, and malton the names of species belonging to the group; the termination *ose* being confined to the glucoses.

Isolation of Sugars.

The general methods by which sugars are isolated in the proximate analysis of animal and vegetable substances depend much on the nature of the associated bodies (see par. 554). Principles of separation commonly utilised are:—the removal of albuminoid bodies by heat or precipitation; the precipitation of dextrin and other gummy matters by alcohol; the removal of organic acids and various other matters by acetate of lead; concentration of the saccharine fluid with a view to promoting crystallisation; and the detection and estimation of the sugars present by their reactions as reducing agents (page 223), and their relations to polarised light. A third mode of determination is based on the specific gravity of the saccharine solution. Other useful processes for estimation or differentiation are based on the behaviour of the sugars with yeast, and on treatment with concentrated and dilute acids, &c. These general methods will be described in the following sections, before dealing with the special application of these and other processes to the examination of particular sugars or saccharine substances.

454. RELATIONS OF THE SUGARS TO POLARISED LIGHT.

The greater number of sugars possess the property of altering the plane of polarisation of a ray of light. The power is possessed not merely by the solid sugars but also by their solutions, the rotatory action exerted by the latter being approximately, but not strictly, proportional to their concentration, or in other words to the number of molecules of dissolved sugar which the ray of light is caused to traverse.

The principle of construction of polarimeters, and the optical activity of various organic substances are described at length in pars. 47 to 63.

455. Specific Rotatory Powers of Sugars.

The strength of a cane-sugar solution which will produce the same deviation, when examined in a tube 2 decimetres in length, as a plate of quartz 1 millimetre in thickness, has been determined by various observers. Clerget estimated it at 16·471 grammes of sucrose in each 100 c.c. of solution. Dubrunfaut reduced the amount to 16·390 grammes, while the weight 16·350 grammes was the result of the investigations of a commission consisting of Pouillet, Barreswil, Schlösing, and Dubosq. The directions now issued with the instrument specify the last-named amount as that to be used in verifying the scale. Recently Girard and De Luynes have given 19·190 grammes of cane sugar per 100 c.c. as the equivalent of 1 millimetre of quartz. Tollens (*Ber.*, 1877, 1403), in a very elaborate paper, gives 16·337 grammes as the standard amount.[1] The deviation of the D line produced by 1 millimetre of quartz is 21° 40′, according to Broch, or 21° 48′ according to Girard and De Luynes. The mean of these two determinations is $21° \ 44' = 21°{\cdot}73$. Employing this figure in the formula for specific rotatory power given in par. 59, the value of S_D for cane sugar in solutions containing about 16 grammes per 100 c.c. may be found as follows :—

$$S_D = \frac{100 \times 21°{\cdot}73}{2 \times 16{\cdot}337} = 66°{\cdot}50.$$

456. As stated already, the concentration of the solution sensibly affects the specific rotation of sugars, and not always in the same direction. Thus, strong solutions of sucrose cause a less deviation than the same amount of sugar would in more dilute solutions, while with dextrose the reverse is the case. On this account, recorded values for S must not be interpreted too strictly

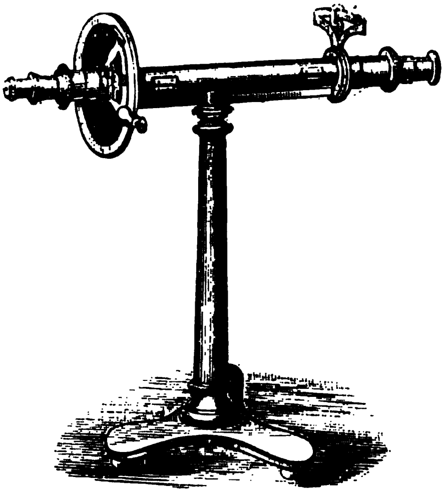

Fig. 10.[2]

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[1] The corresponding amount for the Ventzke-Soleil instrument is 26·086 grammes in 100 c.c.

[2] The accompanying illustration (fig. 10) shows the appearance of a new instrument of the Laurent type, having an ingenious optical modification due to Mr Thos. Bayley. It has given satisfaction in the hands of the writer and others, and is obtainable at a comparatively moderate price from P. Harris & Co., Birmingham.

in cases in which no mention is made of the concentration of the solution. The importance of this point is well shown by the following determinations by Hesse[1] of the value of S_D for cane sugar in solutions of various strengths:—

Grammes of Sucrose per 100 c.c.	Value of S_D.
1	67·95
2	67·39
3	67·05
6	66·67
10	66·50
20	66·45

The exact apparent specific rotatory power may be found, for solutions of strengths varying from 1 to 10 grammes of cane sugar per 100 c.c., by the following formula, in which c represents the number of grammes of sugar in each 100 c.c. of the solution: $S_D = +68{\cdot}65 - {\cdot}828c + {\cdot}115415c^2 - {\cdot}00541666c^3$. Beyond a concentration of 10 grammes of sugar per 100 c.c. of the solution, the decrease is pretty regularly ·005 for each unit of sugar.[2]

457. The values of Tollens and Hesse for the specific rotation of cane sugar agree with those of Tuschmidt, (*Jour. f. Pract. Chem.*, [2] ii. 235) who obtained 66·42 (apparently for somewhat concentrated solutions), and Backhoven, who obtained the same result (*Ibid.* [2] viii. 277). Schmitz, again, has found 66·42 and 66·53 as the value of S_D when $c = 10$ (*Ber.*, 1877, 1414), and, lastly, Tollens (*Ibid.* [2] viii. 1403) gives $+66^\circ{\cdot}48$ as the correct value for $S_{D_{10}}$ in the case of cane sugar. These results all correspond closely, and point conclusively to a value of $+66^\circ{\cdot}5$ for cane sugar in solutions of a concentration from 10 to 20 grammes per 100 c.c. It must be remembered that this is the *apparent* specific rotation for the concentration in question; the *absolute* value of S_D for cane sugar being, according to Tollens, $+63^\circ{\cdot}90$, and according to Schmitz, $+64^\circ{\cdot}16$.

458. Although the apparent specific rotatory power of cane sugar for the D line may be considered to be accurately ascertained, the same cannot be said of the value for the transition-tint. This

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[1] *Annal. der Chemie*, clxxvi. 95. These determinations have been recently disputed by Tollens, who finds a very slight *increase* in the rotatory power of very dilute solutions (*Ber.*, xvii. 1751).

[2] Calculated from the formula in the text the value of S_D for cane sugar when $c = 10$ is $66^\circ{\cdot}4948$. Tollens has recently proposed the formula $S_D = 66{\cdot}386 + 0{\cdot}015035c - 0{\cdot}0003986c^2$. By this, if $c = 10$, $S_D = 66{\cdot}4966$.

is doubtless due in part to the fact that the transition-tint is not a ray of definite refrangibility, and even differs with different observers.

These are insurmountable difficulties in the way of obtaining a constant value for S_j, and hence all determinations made by instruments intended for observing the transition-tint must be regarded as of secondary value only. This is well shown by the discordant factors proposed by different observers for calculating S_D to S_j in the case of cane sugar.[1]

The mean of the more trustworthy of these determinations gives a value for S_j not greatly different from $+73°·8$, which is that generally adopted. If this be accepted as the specific rotation of cane sugar for the transition-tint, then S_D and S_j may be calculated into each other by the following factors, which are those adopted in this work :—

$$\frac{S_j}{S_D} = \frac{73·8}{66·5} = 1·110 \text{; and } \frac{S_D}{S_j} = \frac{66·5}{73·8} = ·9011.$$

459. In the following table are given the most reliable determinations of specific rotation of some more important species of sugars. The optical properties of the rarer sugars are shown in the

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[1] The following figures illustrate this fact. For convenience, the value of S_D is uniformly taken at $+66°·5$, and the product obtained by multiplying this constant by the factor or fraction represents the value of S_j.

S_D ×	Factor	=	S_j		Authority.
66·5 ×	1·129	=	75·08	. .	Landolt; Montgolfier.
	$\frac{24}{21·67}$	=	73·65	. .	Broch.
	$\frac{24}{21·80}$	=	73·21	. .	Girard and De Luynes.
	$\frac{24}{21·54}$	=	74·09	. .	Brown and Heron.
	1·091	=	72·55	. .	Calderon.
	1·049	=	69·96	. .	Weiss.

The factor of Calderon is remarkable. It is deduced from determinations made by him in Berthelot's laboratory with the view of revising that chemist's value for $S_j (= 73·8°)$. Calderon found, for 10 to 20 per cent. solutions of cane sugar, $S_D = 67·1$ and $S_j = 73·2$ (*Compt. rend.*, lxxxiii. 393). Brown and Heron do not state the grounds of their adoption of the ratio employed by them. Holzer (*Ber.*, xv. 1938) gives the factor of Weiss as 1·034, which is even more anomalous than the value given in the table. Holzer found that the value of S_D was not materially affected by the addition of picric acid or other colouring matters to the solution, but when white light was employed the rotation was affected in a very marked degree.

tables on page 189 *et seq.*[1] It will be observed that the figures given below are the *apparent* or *sensible* specific rotatory powers *for solutions containing* 10 *per cent. or so* of the solid sugar. The figures printed in bolder type are the result of direct determinations, the others being calculated by means of the ratio—

$$\frac{S_j}{S_D} = 1{\cdot}11.$$

It is not certain, however, that this ratio is correct in its application to all species of sugar. The signs + and − signify *dextro-* and *lævo*-rotation respectively. It must not be forgotten that the crystals of sugars (other than cane) are not usually anhydrous when deposited from aqueous solutions. The formulæ given in the following table show the condition of hydration of the sugars to which the values for specific rotation apply :—

Species of Sugar.	Formula.	Apparent Specific Rotatory Power.		Reference.
		S_D.	S_j.	
Cane sugar, .	$C_{12}H_{22}O_{11}$	**+ 66·5**	**+ 73·8**	See par. 455.
Maltose, . .	$C_{12}H_{22}O_{11}$	**+139·2**	**+154·5**	See par. 608.
Milk sugar, .	$C_{12}H_{22}O_{11}+H_2O$	**+ 52·7**	+58·5	See par. 649.
Galactose, .	$C_6H_{12}O_6$	**+ 81·3**	+90·2	See par. 677.
Sucro-dextrose,	$C_6H_{12}O_6$	**+ 52·7**	**+ 58·5**	See par. 667.
Lævulose, .	$C_6H_{12}O_6$	−98·8 at 15° C.	−109·7 at 15° C.	Deduced.
		−52·7 at 87°·2 C.	− 58·5 at 87°·2 C.	See next page.
Invert sugar, .	$2C_6H_{12}O_6$	−23·65 at 15° C.	**−25·6** at 15° C.	See below.
		− 0 at 87°·2 C.	**− 0** at 87°·2 C.	

The values given in the above table are those for the rotations produced by solutions of the various sugars which have been heated or kept for some hours. If this condition be not observed, the curious phenomenon of bi-rotation will cause the results to be considerably higher (par. 483). It is not improbable that some of the discrepancies in the observations of the specific rotations of certain of the sugars originated in a neglect of this precaution.

According to Tuschmidt, Casamajor, and many other observers,[2] a solution of cane sugar which, *before* inversion, shows a deviation of + 100 divisions, *after* inversion has a lævo-rotation of − 36·5 divisions at 15° C.

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[1] According to Thomsen the rotatory power of the carbohydrates in solutions of infinite dilution ($c=0$), multiplied by the molecular weight, is always some multiple of the constant number 19 (*Jour. Soc. Chem.* xl., 245), but his views have not met with very general acceptance.

[2] As expressed in the text the statement is Casamajor's. Tuschmidt gives the formula : $S_t = -(27{\cdot}6 - 0{\cdot}32t)$. That is, the rotatory power of invert sugar is −27°·6, less 0°·32 for each degree centigrade above zero. Thus, at 15° C. the rotation would be $-27{\cdot}6-({\cdot}32\times15) = -22^\circ{\cdot}8$, against $-23^\circ{\cdot}05$, the number adopted in the test.

The value given in the table for the specific rotation of invert sugar is based on this fact, also taking into account the increase in the weight of solids caused by the inversion of the cane sugar to glucoses.[1]

From the value for invert sugar thus found, that of lævulose was calculated by the equation, $25{\cdot}6 \times 2 + 58{\cdot}5 = 109{\cdot}7$.[2]

PRACTICAL OPTICAL SACCHARIMETRY.

460. For the application of the rotatory action exerted by sugars and allied bodies on a ray of polarised liquid to the examination of saccharine substances, it is necessary that the body shall exist in solution, and that the solution be free from suspended matter and also fairly free from colour, though this last condition is less essential with the instruments with which a sodium lamp is used than with those which employ white light.

It will be convenient first to describe the method of estimating cane sugar in a commercial product containing no other optically active substance, after which its determination in presence of invert sugar will be dealt with (par. 471), and subsequently the employment of the polarimeter for estimating other kinds of sugar (par. 479) will be described.

461. Polarimetric Determination of Sucrose in the Absence of other Optically Active Bodies.

For the purposes of saccharimetry, it is found convenient in practice to employ a constant weight of each sample. The weight to be taken varies from 16·19 to 26·07 grammes, according to the instrument to be employed, and to a lesser degree with each particular instrument. With Soleil's saccharimeter the standard weight is 16·350 grammes, and with other instruments, showing directly the percentage-content of real sugar in the sample, weights closely approximating to 16·337 grammes are usually employed. With polarimeters furnished with the Ventzke scale, however, the

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[1] The equation used was :—

$$\mathrm{Sj} = \frac{-36^\circ{\cdot}5 \times \dfrac{{\cdot}2173 \times 73{\cdot}8}{66{\cdot}5}}{2 \times \dfrac{16{\cdot}337}{100} \times \dfrac{100}{95}} = -25{\cdot}59^\circ \text{ at } 15^\circ \text{ C.}$$

[2] The corresponding value for 14° C. is − 110°·5, against − 106° as generally taken.

standard weight is 26·048 grammes.[1] With instruments employing sodium light, and graduated only in angular degrees, 18·800 grammes is a more convenient weight to use.

462. Preparation of the Solution of Sugar for the Polarimeter.

Having carefully mixed the sample to obtain a fair average specimen, the standard quantity is weighed out and introduced carefully into a 100 c.c. flask. About 50 c.c. of water are then added, and the liquid carefully agitated until the whole of the sugar has passed into solution.

If the liquid be clear and colourless it is merely necessary to dilute the liquid to exactly 100 c.c., mix it well by agitation, and at once introduce it into the tube of the polarimeter. But if the liquid be coloured to any notable extent, as is usually the case with commercial sugars, it is essential that it should be decolorised before being submitted to optical examination. The necessary clarification may be effected by means of animal charcoal, hydrated alumina, or basic acetate of lead.

463. Animal charcoal is employed by adding to the solution of the sugar (prepared as above described, and diluted to exactly 100 c.c.) about one-fourth of its bulk of powdered bone-black, which must be fresh and free from hygroscopic water. The liquid is well agitated with the black for a few minutes and then passed through a dry filter. This is a preferable mode of using charcoal to the French plan, in which the granular bone-black is placed in a vertical tube closed at the lower end by a plug of cotton-wool, and the sugar solution passed through the column of charcoal. In using this method, the first portions of the percolated liquid must be rejected, as the charcoal absorbs sugar as well as colouring matter. It is highly probable that the tendency to absorption is the cause of many of the discrepancies in sugar assays, but by making the optical determination on the latter portion of the percolate the error due to the absorption of sugar by the charcoal may be completely eliminated.

464. The source of error may be avoided altogether by employing the following method of clarification, which is very efficacious even under extremely unfavourable conditions:—Weigh out the normal quantity of sugar and dissolve it in about 50 c.c. of water in a flask holding 100 c.c., as described in par. 462. According

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[1] In the original Soleil-Ventzke instruments the scale was so divided that a solution of cane sugar, of a density of 1·10 at 17°·5 C., observed in a tube 20 centimetres in length, rotated 100 divisions. A solution of sugar of the above density is obtained by dissolving 26·048 grammes in water and diluting the liquid to 100 c.c.

to the quality of the sample, the solution will be (1) colourless but cloudy, (2) yellow, (3) brown, or (4) almost black. In the first case, add about 3 c.c. of a cream of hydrated alumina and one drop of basic acetate of lead solution.[1] In the second case, the same volume of alumina may be used, but the lead solution increased to 3 or 5 drops. In the third or fourth case add about 2 c.c. of a 10 per cent. solution of sodium sulphite, and then the lead solution gradually, with constant shaking, till no further precipitate is produced.[2] Whichever mode of clarification be adopted, the liquid is well agitated, and allowed to stand at rest for a few minutes, to ensure the complete separation of any precipitate. The flask is then filled nearly to the mark with water, and the froth allowed to rise to the surface, when it is destroyed by the cautious addition of a few drops of spirit or a single drop of ether. Water is then added exactly to the mark, the contents of the flask thoroughly mixed by agitation, and the liquid filtered through a dry filter.

465. Another mode of clarification, recommended by Scheibler, and very simple and good in all ordinary cases, is as follows:—Solutions of alum or aluminium sulphate and of basic lead acetate are prepared of equivalent strengths, so that on mixing equal measures and filtering no sulphate remains in solution. To the solution of sugar 5 c.c. of each of these liquids is added, the mixture shaken, made up to 100 c.c., and passed through a dry filter.

466. Some exceptionally dark cane sugars, and most beet-root molasses, are not sufficiently decolorised by either of the above methods. In such cases a double normal quantity should be weighed out, and the solution clarified by sodium sulphite and basic lead solution, as before described, a rather larger quantity of the latter liquid being employed. The solution is made up accurately to 100 c.c., filtered, and 50 c.c. of the filtrate treated with a saturated

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[1] This alumina cream is prepared by pouring a solution of alum into excess of a hot solution of washing-soda, collecting the precipitate in a linen bag, washing well with boiling water, and mixing it with enough water to form a thin cream.

The solution of basic acetate of lead is prepared by grinding together in a mortar ½ lb. of recently ignited litharge, 1 lb. of acetate of lead, and enough water to render the whole pasty. The mixture is next boiled with three pints of water, and the solution filtered and preserved in well closed bottles.

[2] If, as is often recommended, a considerable excess of lead solution be added, some of the precipitate is apt to be redissolved, and the solution becomes opalescent and filters with difficulty. The presence of lead in the solution is said to effect the results, having a tendency to cause somewhat excessive readings, though the lead solution itself has no optical activity.

solution of sulphurous acid[1] until the liquid smells strongly of the gas. About 2 grammes of purified animal-charcoal[2] are then added, the liquid well shaken, made up exactly to 100 c.c., and filtered. By proceeding in this manner, a perfectly colourless or lemon-yellow solution may be obtained from the worst samples.[3]

467. METHOD OF EMPLOYING THE POLARIMETER.

The solution of sugar having been clarified, if necessary, by one of the foregoing methods, the tube of the polarimeter (2 decimetres in length) is rinsed with a little of it, and then completely filled with the liquid. A glass plate is then cautiously placed on the top, and secured by screwing home the brass cap. This being done, the cap should be somewhat loosened to avoid any chance of pressure being exerted on the contents of the tube. The tube with its contained saccharine solution is then placed between the polariser and analyser of the saccharimeter, when an optical disturbance will be observed, the extent of which will depend on the amount and nature of the sugar in solution.

The polarimeter is then adjusted until the neutral point is reached, or, in other words, until the optical disturbance produced by the introduction of the saccharine solution is compensated. The rotation required to produce this effect is then read off and recorded.

Polarimeters intended for use in saccharimetry are usually graduated so that the percentage of cane sugar in the sample examined is shown without calculation, which is not the case if the instrument be graduated in circular degrees only.

468. According to Biot, a plate of quartz 1 millimetre in thickness produces rotation of exactly 24 circular degrees for the transition-tint. This rotation is taken as the standard in the Soleil and Soleil-Duboscq saccharimeters, and the 24 degrees are divided into 100 equal parts, so that each one of the divisions is equivalent to 0·24 circular degrees. A cane sugar solution contained in a 2-decimetre tube must have a concentration variously estimated at 16·19 to 16·35 grammes in 100 c.c. of the liquid to produce a rotation equal to that caused by 1 millimetre of quartz.

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[1] Instead of employing a saturated solution of sulphurous acid it is convenient to bubble through the liquid a little sulphur dioxide, now sold in syphons by Boake & Co.

[2] This is prepared by boiling 1 lb. of freshly ground bone-charcoal in half a gallon of common yellow hydrochloric acid diluted with one gallon of water. The liquid is filtered through a linen bag, and the residue washed with hot water till free from acid, dried, and ignited to full redness in a closed crucible. It is bottled while still warm, and kept carefully dry.

[3] The additional precautions necessary to free beet-root juice and molasses from traces of foreign optically active bodies are described in pars. 589 and 590.

In practice, a solution of sugar, varying in strength from 16·190 to 16·350 grammes of the solid in each 100 c.c. according to the practice of the instrument maker, is introduced into the polarimeter, and the point of neutrality marked as 100. The distance between this point and the zero point is then divided into 100 equal parts. Hence with each particular saccharimeter should be employed a solution of sugar of the same concentration as that used for its graduation. By doing this the percentage of cane sugar contained in any impure sample free from other active bodies can be ascertained by dissolving the standard weight to 100 c.c. and noting the number of divisions through which the light is rotated when the solution is interposed in a 2-decimetre tube. The saccharimeters employing sodium-light are usually graduated in a similar manner, but the 100 divisions correspond to about 21·73 angular degrees, instead of 24° as in those instruments using the transition-tint. In all cases it is desirable to verify the standard weight of sugar said to cause a rotation through 100 divisions of the scale, and, if proved correct, this weight should be invariably employed in subsequent experiments. As stated in par. 455, 16·337 grammes for 100 c.c. is the exact quantity of sugar producing a rotation in a 2-decimetre tube equivalent to that caused by 1 millimetre of quartz, and this quantity will be the same whether the instrument be constructed for the sodium-light or for the transition-tint.

469. Most instruments are now graduated both in circular degrees and in percentages of cane sugar. If the polarimeter employed be graduated in the former manner only, the percentage of real sugar in a sample may be ascertained by comparing the rotatory power of its solution with that of an equally concentrated solution of pure cane sugar.[1] Thus, if the solutions be made by dissolving in water 20 grammes each of the standard sugar and the sample, and making the liquids up to 100 c.c. each, then, in a 2-decimetre tube the standard solution should give an angular rotation of $+26{\cdot}6$ degrees for the sodium ray.[2] Hence, if the angular rotation produced by the solution of the sample was only 25·5 degrees, the percentage of sugar contained in it was 95·87, according to the proportion

$$\frac{25{\cdot}5 \times 100}{26{\cdot}6} = 95{\cdot}87.$$

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[1] Sugar crystals, or white sugar-candy, crushed to powder, and dried first by pressure between layers of filter paper, and then by exposure for a short time to a temperature of 100° C., will furnish a very good standard.

[2] According to the equation in par. 59, $66{\cdot}5 = \frac{100\,a}{l \times c} = \frac{100\,a}{2 \times 20}$; whence $a = 26{\cdot}6$.

Even this simple calculation may be avoided, for, if the weight of the sample taken be $\frac{25 \times 20}{26 \cdot 6} = 18 \cdot 800$ grammes, the angular rotation produced in a 2-decimetre tube will be exactly 25 degrees for the D line, and hence each degree of angular rotation will represent 4 per cent. of sugar in the sample.

470. *For the determination of sucrose in saccharine liquids*, such as cane and beet-juice, the formula in par. 59 becomes

$$c = \frac{a \times 100}{l \times S}.$$

For S should be substituted either 66·5 or 73·8, according as the instrument employs the sodium ray or white light. Thus, if the liquid has caused an angular deviation of 19°·0 when examined in the 2-decimetre tube with a Laurent instrument, then :—

$$c = \frac{19 \times 100}{2 \times 66 \cdot 5} = \frac{1900}{133} = 14 \cdot 29.$$

Therefore, the juice contained 14·29 grammes of cane sugar in each 100 c.c.

If the polarimeter be merely graduated in sugar-units the strength of juice will be found by multiplying the units of sugar indicated by the standard weight of sugar with which the instrument is intended to be used, and dividing the product by 100. Thus, if with a Ventzke instrument a rotation equal to 72 sugar units has been observed, then :—

$$\text{Concentration} = 72 \times \frac{26 \cdot 048}{100} = 72 \times \cdot 26048 = 18 \cdot 76.$$

471. Determination of Sucrose in presence of Glucose. Clerget's Process.

While the polarimeter is capable of accurately indicating the proportion of cane sugar present in a liquid containing no other optically active substance, its readings may be below the truth, or actually negative, if the liquid contain a notable amount of certain other varieties of sugar, or other active bodies. Hence, in such complex liquids the direct reading of the polarimeter is erroneous, but by operating in a manner first suggested by Clerget the indications may still be relied on.

472. The different varieties of glucose are unaffected by heating with dilute acid, while cane sugar is, by such treatment, converted into a mixture of equal parts of sucro-dextrose or dextro-glucose, and sucro-lævulose or lævo-glucose. $C_{12}H_{22}O_{11} +$

$H_2O = 2C_6H_{12}O_6$. The product is called inverted or invert sugar, of which 100 parts are produced by the hydration or "hydrolysis" of 95 parts of cane sugar.

While the effect of increase of temperature on the rotatory power of cane sugar and sucro-dextrose is almost inappreciable, in the case of lævulose the temperature is a most important factor. The same remark applies to invert sugar, the lævulose of which diminishes in rotatory power to the same extent as if it were unmixed with dextrose. On this account the rotatory power of invert sugar decreases regularly with increase of temperature till at 87°·2 C. it is optically *neutral*, and at still higher temperatures exerts a *dextro*-rotatory power.

473. Serious discrepancies exist in the rotatory power of sucro-dextrose as determined by different observers (see par. 677), but fortunately any doubt as to the true rotatory power of this sugar does not affect the accuracy of ordinary sugar assays, for the change in rotatory power caused by the inversion of a solution of cane sugar has been accurately ascertained, irrespective of the exact measure of the rotatory powers of the two glucoses to the combined influence of which the effect is due. It has been found by various observers that a solution of cane sugar which *before inversion* causes a deviation of 100 divisions to the right, *after inversion* has a *lævo*-rotatory power of 39 divisions at 10° C., and consequently has undergone an optical change equivalent to a *rotation through* 139 *divisions*. Owing to the diminished optical power of lævulose at high temperatures, the change by inversion is less the higher the temperature at which it is observed, decreasing by one division for each increase of 2° C. Thus at 0° C. the change by inversion would equal 144 divisions, and the value for any higher temperature may be found by the equation :—

$$D = 144 - \frac{t}{2}.$$

Hence at 15° C., the change by inversion is 136·5 divisions for a solution previously reading + 100 ; or the number representing the change by inversion, *however expressed*, multiplied by the factor $\cdot 7326 \left(= \frac{100}{136 \cdot 5}\right)$ shows the corresponding rotation caused by the sucrose in the original solution, whence its proportion of cane sugar may be readily deduced.

474. The above factor and equation may be conveniently combined as follows :—C is that part of the rotation produced by the uninverted liquid which is really due to the cane sugar contained

in it, and D is the *change* in the polarimetric reading caused by the process of inversion. Then :—

$$C = \frac{100\,D}{144 - \frac{t}{2}}$$

Thus, if a saccharine solution show at 16° C. a rotation of + 23·0 circular degrees before inversion, and after inversion a *lævo*-rotatory action of 7·2 degrees at 16° C., then by the equation :—

$$C = \frac{100 \times 30{\cdot}2}{144 - \frac{16}{2}} = \frac{3020}{136} = 22^{\circ}{\cdot}26\,.$$

Thus of the 23 circular degrees of rotation produced by the original sugar solution 22°·26 were really due to cane sugar, and should be calculated to that substance, while the remaining + 0°·74 of rotation was due to dextrose or some other *dextro*-rotatory substance not capable of inversion by the means employed for the purpose.

475. In employing the foregoing method of examining saccharine liquids containing any considerable quantity of invert sugar, it is essential that the temperature at which the observation of the original rotation was made should be identical with that at which the reading of the inverted solution is taken, otherwise an error would be produced from the altered optical activity of the invert sugar originally present. Some observers have held that the invert sugar present in raw cane syrup is optically inactive, but this statement has been disproved by Meissl.

The rotation due to cane sugar having been ascertained, the amount of that substance present in the solution may be found as described in par. 470.

476. In the above arguments the fact is left out of consideration that inversion usually involves increase in the bulk of the saccharine liquid. In practice, the increase is neutralised by taking the reading of the *inverted* sugar in a tube 22 centimetres in length instead of 20, as with the original liquid. The 22 centimetre tube, intended for the observation of the rotation of the inverted sugar, should be furnished with a short vertical tube to allow the insertion of a thermometer, so that the temperature of the liquid during the observation may be accurately ascertained.[1]

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[1] The increase in the volume of the solution can be avoided by inverting with crystallised oxalic acid. A good way of avoiding change of temperature is to employ a polarising tube surrounded with cold water, on the plan of a Liebig's condenser.

477. **The Inversion of Sugar** for polarimetric puposes is best accomplished in the following manner:—The sugar solution is clarified and made up to a definite volume in the manner described in par. 462 *et seq.*, and its rotating power observed by the polarimeter. 50 c.c. of the solution are then mixed with 5 c.c. of pure fuming hydrochloric acid of about 1·16 sp. gravity. This is best done in a flask having two marks on the neck, one at 50 c.c. and a second at 55 c.c. The flask is next heated on a water-bath till its contents have acquired a temperature of 68° C., an operation which should be arranged to occupy about ten minutes. The solution is then cooled down by immersing the flask in cold water, and if coloured, may be shaken with a very little bone-black and filtered. The liquid is then poured into the 22 centimetre tube, and its rotation observed by the polarimeter in the manner already described. (For other methods of inversion, see par. 502 *et seq.*)

478. Clerget's method is applicable to the estimation of cane sugar in such complex saccharine liquids as contain no bodies other than cane sugar, the optical activity of which is modified by heating with dilute acid under the conditions sufficient to insure the inversion of cane sugar. But it must be borne in mind that instances may occur in which such changeable substances are present. Thus the mixture of dextrose, maltose, and dextrin known as "starch-sugar" undergoes a change in optical activity by heating in solution with dilute acid, and there exist in molasses sensible quantities of optically active bodies, which may undergo modification by treatment with acid. Hence the results of Clerget's method must be received with caution when applied to such products.

It must also be borne in mind that the presence of various substances, themselves optically inactive, has a tendency to modify the rotatory powers of saccharine liquids, though interference from this cause is not likely to occur in practice.[1]

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[1] The presence of alcohol in solutions of cane sugar does not materially alter the rotatory power, but it reduces the rotation of invert sugar. Free caustic alkalies notably reduce the rotation of saccharine solutions, but on neutralisation with acetic or phosphoric acid the original optical activity is restored. Baryta, strontia, and lime also lower the rotating power of sugar solutions. The neutral carbonates of the alkali metals have but a slight influence, and the acid carbonates none at all. Chloride of sodium present in equal quantity to the cane sugar in a 10 per cent. solution of the latter, reduces the rotation from 67°·0 to 65°·3; and in a solution containing 20 grammes of sugar and 20 of salt per 100 c.c. the rotation is only 61°·0. According to Muntz, the sulphates, nitrates, phosphates and acetates of the light metals alter the polarimetric reading from 2 to 3 per cent., when they are present in the proportion of 20 or 30 parts to 100 of sugar.

479. Polarimetric Determination of Sugars other than Sucrose.

The optical estimation of all rotating sugars may be effected on principles similar to those already described for determining sucrose, provided that no interfering substance be present. The method of clarifying coloured solutions is in all cases much the same as that found effective with cane sugar (par. 463 *et seq.*), and the directions need not be repeated.

480. In *preparing solutions* of sugars other than sucrose for examination with the polarimeter, if the instrument is merely graduated in cane-sugar units it is desirable to employ the ordinary standard weight of sugar, but the indications require to be translated into those of the particular species of sugar under examination. This may be done by multiplying the observed sugar-indication by 66·5, the value of S_D for cane sugar, and dividing it by the specific rotatory power (S_D) for the sugar under treatment. The concentration of solutions of unknown strength may similarly be ascertained.

481. When an instrument graduated in circular degrees is used, it is simpler to make a solution containing 20 grammes of the sugar per 100 c.c., and examine it in the usual way in a thickness of 2 decimetres. The percentage of sugar in the sample will then be found by dividing the specific rotatory power into the circular angle of rotation, and multiplying the number thus obtained by 250.[1]

482. INFLUENCE OF TEMPERATURE, REACTION, &c.

In examining solutions of sugars with the polarimeter, it must be borne in mind that the optical activity of certain species of sugars is modified more or less by the temperature, concentration, and other circumstances already alluded to. Hence, to ensure the best results, the solution should have a concentration of from 10 to 20 grammes per 100 c.c., and the temperature should be as near 15° C. as possible, unless some other temperature be deliberately chosen, and its effects duly allowed for. The presence of free acid in moderate amount does not influence the rotatory power of sugars, but any alkaline reaction must be carefully neutralised before taking the observation.

483. BI-ROTATION is a term employed to signify the curious change in optical activity which is undergone by the solutions of certain sugars when kept or heated. The change in optical activity is probably due to the existence of two modifications of

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[1] $c = \frac{100\,a}{2 \times S}$. This gives the pure sugar in 100 c.c. of the solution or in 20 grammes of the sample, and the percentage will be five times this.

bi-rotating sugar, α and β, the first of which is present in freshly-made solutions, but undergoes conversion into β in the course of a few hours at the ordinary temperature, or immediately on heating the liquid. In some cases (*e.g.*, dextrose and milk sugar), the freshly-made solution has a greater optical activity than after keeping, whilst in others (*e.g.*, maltose) the rotation increases on standing. To avoid the error due to bi-rotation, the solution of a solid sugar (other than sucrose) should always be heated to boiling before introducing it into the observing tube. It is desirable to heat the solution before finally making it up to an exact volume.

SPECIFIC GRAVITY OF SACCHARINE SOLUTIONS.

484. An aqueous solution of cane sugar, containing 10 grammes of the solid in each 100 c.c., has a density of 1·038·6 at 15°·5 C. (=60° F.). The weight of water in 100 c.c. of this solution is $103{\cdot}86 - 10{\cdot}00 = 93{\cdot}86$ grammes. As this would occupy 93·86 c.c., the volume occupied by the 10 grammes of sugar is 6·14 c.c., whence the specific gravity of the sugar in a state of solution is $\frac{10}{6{\cdot}14} = 1{\cdot}628$,—a figure which agrees closely with those obtained in a similar manner for other carbohydrates.

485. From careful determinations it appears that solutions of equal strengths containing different carbohydrates have approximately the same, though not strictly identical, specific gravities. In other words, the density of the solution depends chiefly on the amount of solid dissolved, and *not* on the percentage of carbon in the liquid. As a consequence of this fact, it is found that solutions of cane sugar increase very sensibly in density on inversion by dilute acid, or a small quantity of yeast, and a similar increase of density is observed by the hydrolysis of maltose.[1]

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[1] The increase in the density of cane sugar solutions by inversion has a practical bearing of an unpleasant character, as some brewers have discovered to their cost, the duty on worts being levied on the content of saccharine matter as indicated by the specific gravity. Hence, if, from the presence of traces of acids or ferments, the dissolved sugar gradually undergoes inversion, the brewer will be liable to an increased duty. Occasionally he has been charged with having surreptitiously added more sugar to his wort, though the real nature of the change ought to be known to the Excise. Direct estimation of the solid matter in the solution appears to confirm the calculation from the density, owing to the fixation of the elements of water in the inversion of the sugar. By completely inverting the solution with acid (making due allowance for the increase of density due to the acid used), calculating the sugar from the

486. The following table shows the specific gravity of solutions of sugars and allied substances under three different conditions, namely :—

(*a*) Solutions containing 4·21 per cent. of carbon, which is the proportion present in a solution containing 10 per cent. by weight of cane sugar ;

(*b*) Solutions containing 10 grammes of the solid in 100 grammes *weight* of liquid ; and,

(*c*) Solutions containing 10 grammes of the solid in 100 c.c. *measure* of the solution.

The figures refer in all cases to densities at 15°·5 C. (=60° F.), water at the same temperature being taken as 1000.

Substance in Solution.	Formula.	Specific Gravity of Solutions containing			Observer.
		a 4·21 per cent. of Carbon.	*b* 10 grs. solid per 100 grs.	c 10 grs. solid per 100 c.c.	
Dextrose, . . .	$C_6H_{12}O_6$	1042·1	1040·0	1038·5	F. Salomon.
Starch glucose, . .	...	1042·0	1039·9	1038·4	A. H. Allen.
Invert sugar . .	2 $C_6H_{12}O_6$	1042·4	1040·3	1038·8	G. H. and R.[1]
		1042·1	1040·0	1038·5	A. H. Allen.
		1042·3	1040·2	1038·7	Chancel.
Milk sugar, . .	$C_{12}H_{22}O_{11}$	1040·6	1040·6	1039·1	O. Hehner.
Cane sugar, . .	$C_{12}H_{22}O_{11}$	1040·6	1040·6	1039·0	G. H. and R.[1]
		1040·3	1040·3	...	Brix ; Gerlach.
		1040·1	1040·1	1038·6	Brown and Heron.[2]
Maltose, . . .	$C_{12}H_{22}O_{11}$	1040·8	1040·8	1039·3	Brown and Heron.[2]
		1040·0	1040·0	1038·5	O'Sullivan, 1876.[3]
		1041·1	1041·1	1039·5	O'Sullivan, 1879.[3]
Malt extract, .	...	...	1038·9	1037·5	Chas. Graham.
		...	1040·4	1038·9	Muspratt.
,, pale, .	...	1041·2	...	...	G. H. and R.[1]
,, brown, .	...	1041·2	...	...	G. H. and R.[1]
Dextrin, . . .	$xC_{12}H_{20}O_{10}$	1038·3	1040·0	1038·5	O'Sullivan, 1876.[3]
		1039·0	1041·1	1039·5	O'Sullivan, 1879.[3]
		1039.2	1041·0	1039·4	H. T. Brown, 1884.
Starch paste, . .	$yC_{12}H_{20}O_{10}$	1039·1	1041·3	1039·7	Brown and Heron.[2]
Caramel, . . .	$C_{12}H_{18}O_9$(?)	1034·9	1039·0	1037 5	G. H. and R.[1]

density and deducting $\frac{1}{20}$ for increase of gravity due to inversion, the amount of sugar which was present in the wort may be ascertained.

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[1] *Report on Original Gravities*, 1852, by Graham, Hofmann, and Redwood.

[2] *Jour. Chem. Soc.*, xxxv. 569 *et seq.*

[3] O'Sullivan's original figure for the solution-density of maltose was 1038·5 (*Jour. Chem. Soc.*, xxx. 130), and he adopted the same figure for dextrin ; but in a recent letter this chemist informs the writer that he now takes 1039·5 as the density of solutions of maltose and dextrin containing 10 grammes of the solid per 100 c.c., the lower figure being a consequence of the extreme difficulty of obtaining these carbohydrates in a condition of absolute dryness and purity.

487. In practice it is convenient to assume the solution-densities of the carbohydrates in the table to be uniformly 1038·6, for a concentration of 10 grammes per 100 c.c. This is Brown and Heron's figure for cane sugar,[1] and is not far from the mean of the whole table.

488. The density of solutions of dextrin and the chief kinds of sugar being almost identical, it follows that the sum of them present in an aqueous solution may be found approximately by allowing an increase of 3·86 in density for each 1 gramme of sugar or other carbohydrate in 100 c.c. of the liquid. For very dilute solutions of cane sugar this figure is correct,[1] but for those containing more than 12 of solids per 100 volumes, the divisor 3·85 gives still closer results. If W be the weight of the solid carbohydrates in 100 c.c., and D be the density of the solution at 60° F. (compared with water as 1000), then the value of W may be found by the equation—

$$W = \frac{D - 1000}{3{\cdot}85} = (D - 1000) \times {\cdot}2597.$$

From the number thus found for W (= the number of grammes of solids in 100 c.c.) the weight of solid carbohydrates in 100 *parts by weight* of the liquid (w) may be found by multiplying W by 1000, and dividing the product by the density of the liquid :—

$$w = \frac{1000 \times W}{D}.$$

489. By the Inland Revenue Act of 1880, the specific gravity of standard wort was fixed at 1057 at a temperature of 60° F. Hence, such wort contains 14·8 grammes of solids per 100 c.c., or 148 lbs. per 100 gallons ;[2] for—

$$\frac{1057 - 1000}{3{\cdot}85} = 14{\cdot}8.$$

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[1] Brown and Heron (*Jour. Chem. Soc.*, xxxv. 644) have laid down a curve by which the strength of cane sugar solutions can be readily ascertained in all cases of less density than 1150.

[2] It is surprising how difficult it is for an unscientific mind to grasp the true relations between weight and volume. Thus, the provisions of the Inland Revenue Act relating to density were at first wholly incomprehensible to the majority of brewers. A very common fallacy was to suppose that a barrel of wort which weighed 20 lbs. more than the same barrel would if filled with water, must necessarily contain 20 lbs. only of dry extract.

This result gives, by the second equation, 14·0 parts of solids in 100 parts by weight of the liquid; for—

$$w = \frac{14800}{1057} = 14{\cdot}0.$$

For all saccharine solutions of moderate strength the foregoing formulæ will answer every purpose. Solutions of invert sugar respond to the formulæ up to about 20 per cent. of contained solid, but more concentrated solutions should be diluted with a known proportion of water before applying the method.

490. Tables showing the densities of concentrated solutions of cane sugar have been published by Gerlach, Scheibler, Balling, and Brix. The following figures are chiefly those of Gerlach, and will answer every purpose:—

Cane Sugar per cent. by weight.	Sp. Gravity at 17°·5 C.	Cane Sugar per cent. by weight.	Sp. Gravity at 17°·5 C.	Cane Sugar per cent. by weight.	Sp. Gravity at 17°·5 C.
10	*1*·0401	34	*1*·1491	58	*1*·2782
11	·0443	35	·1540	59	·2840
12	·0485	36	·1590	60	·2899
13	·0527	37	·1641	61	·2959
14	·0570	38	·1691	62	·3019
15	·0613	39	·1742	63	·3079
16	·0656	40	·1794	64	·3139
17	·0700	41	·1845	65	·3200
18	·0744	42	·1897	66	·3262
19	·0788	43	·1950	67	·3324
20	·0832	44	·2003	68	·3386
21	·0877	45	·2056	69	·3449
22	·0922	46	·2109	70	·3512
23	·0968	47	·2163	71	·3575
24	·1014	48	·2218	72	·3639
25	·1060	49	·2272	73	·3703
26	·1106	50	·2327	74	·3768
27	·1153	51	·2383	75	·3833
28	·1200	52	·2439	80	·4159
29	·1248	53	·2495	85	·4499
30	·1296	54	·2552	90	·4849
31	·1344	55	·2609	95	·5209
32	·1393	56	·2666	99	·5504
33	·1442	57	·2724		

491. CORRECTION OF DENSITIES OF SACCHARINE SOLUTIONS FOR TEMPERATURE.—In breweries it is often convenient to ascertain the density of the wort at a temperature above that of 60° F. (= 15°·5 C.), in which case the specific gravity as observed by the

hydrometer can be calculated into the corresponding number for a temperature of 60° F. in the following manner:—

To unity add ·004 for every degree of specific gravity above 1000 (g) shown by the hot wort, and ·01 for each Fahrenheit degree of temperature (t) above 60° F. Multiply the sum of these by $\frac{1}{10}$th of the number of Fahrenheit degrees above 60° F., when the product, added to the density of the hot wort, will be a number representing the specific gravity of the liquid at 60° F. The rule is expressed by the following formula:—

$$G=\left(1+\frac{(g-1000)4}{1000}+\frac{t-60}{100}\right)\frac{t-60}{10}+g.$$

Thus, if the wort be found to have a density of 1052·0 at a temperature of 110° F., then by the formula:—

$$G=\left(1+\frac{(1052-1000)4}{1000}+\frac{110-60}{100}\right)\frac{110-60}{10}+1052.$$
$$G=(1+{\cdot}208+{\cdot}5)5+1052.$$
$$G=1{\cdot}708\times5+1052.$$
$$G=1060{\cdot}54.$$

The formula may be simplified if for $g-1000$ be substituted e, the excess of density over 1000 at the observed temperature; and for t be substituted f, the excess of temperature above 60 F. The formula then becomes:—

$$G=\left(1+\frac{4e}{1000}+\frac{f}{100}\right)\frac{f}{10}+g.$$

Corrections of densities of cane sugar solutions for temperature may be made by the same formula.

492. **Saccharometers.**—Various modifications of the hydrometer have been divised and used for ascertaining the density of saccharine solutions. Of these, Baumé's instrument is unfortunately still largely used. The method of interpreting its indications and the confusion caused by its use are described in par. 11.

Bates' Brewers' Saccharometer is much used for testing the strength of beer-worts, and hence it is described on page 273.

493. On the Continent, Balling's Saccharometer is much used. If B = degrees of Balling and b those of Bates, the

indications of one instrument may be calculated to those of the other by the following formulæ :—

$$B = \frac{260b}{360+b}; \text{ and } b = \frac{360B}{260-B}.$$

The saccharometer of Brix is practically the same as that of Balling. In each, the number of degrees is identical with the percentage by weight of cane sugar in the solution. (See par. 490).

ACTION OF STRONG ACIDS ON SUGARS.

494. Sugars having the constitution of aldehydes of polyatomic alcohols, or oxygen-ethers of the same, the general tendency of strong acids, especially organic, is to convert them into ethereal compounds. Thus, by the action of *acetic acid* or *anhydride* on cane sugar, acetyl-derivatives are formed, containing 1, 4, 5, 6 or 8 atoms of the acid-radicle $C_2H_3O_2$, according to the details of the treatment. Mono-aceto-sucrose has the composition $C_{12}H_{21}(C_2H_3O_2)O_{11}$. These acetyl derivatives are true ethers,[1] being saponified by caustic potash with formation of potassium acetate and cane sugar.

495. Action of Nitric Acid.

By the action of *cold*, very *concentrated nitric acid* many of the sugars yield nitric ethers of an explosive character. Thus, the bodies $C_{12}H_{19}(NO_3)_3O_{11}$ and $C_{12}H_{17}(NO_3)_5O_{11}$ are produced by adding milk sugar to a cold mixture of concentrated sulphuric and nitric acids. On diluting the solution with water, the nitric-derivatives are precipitated. If the temperature be allowed to rise, the sugar is oxidised with violence.

496. When heated with *dilute* or *moderately concentrated nitric acid*, the sugars yield oxidation-products, of which mucic, saccharic, tartaric, and racemic acids are the most constant and characteristic. The formation of the isomeric mucic and saccharic acids is represented by the following equation :—

$$C_6H_{12}O_6 + O_3 = C_6H_{10}O_8 + H_2O.$$

Tartaric acid is probably formed by the further oxidation of saccharic acid, and racemic by the oxidation of mucic. Saccharic acid is the product of the action of dilute nitric acid on cane sugar dextrose, mannite, mycose, &c., while mucic acid results from the cautious oxidation of dulcite, melitose, lactose, &c.

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[1] According to Berthelot the products of the action of organic acids on glucose are not glucosides, but ethers of glucosan, $C_6H_{10}O_5$, the elements of water being eliminated.

497. For the preparation of mucic or saccharic acid the sugar should be heated on the water-bath with about 4 times its weight of nitric acid of 1·27 specific gravity, until gas is copiously evolved, when the mixture is maintained at about 60° till it begins to become brown, or the evolution of gas ceases. The liquid is then diluted with half its bulk of water and allowed to stand. On cooling, mucic and oxalic acid will crystallise out, and may be separated by warm alcohol, in which only the oxalic acid dissolves.

498. Mucic Acid forms a sandy crystalline powder or crystalline plates. It requires 66 parts of boiling water for solution, and it is nearly insoluble in cold water or alcohol. The mucates are mostly insoluble, even the neutral potassium salt being only sparingly dissolved by water, but the acid salt is somewhat more soluble.

499. Saccharic Acid remains in the liquid from which mucic and oxalic acid have crystallised out. The solution should be neutralised by potassium carbonate, strongly acidulated by acetic acid, and allowed to stand, when the sparingly soluble acid potassium saccharate crystallises out in brownish crusts. By re-crystallising this salt, neutralising the solution with potash, precipitating with cadmium sulphate, and decomposing the insoluble cadmium saccharate by sulphuretted hydrogen, a solution is obtained which on evaporation yields saccharic acid as an amorphous deliquescent substance, easily soluble in alcohol.

500. By treatment with *hot concentrated nitric acid*, the sugars undergo oxidation to more simple products, such as oxalic acid, $C_2H_2O_4$, and carbonic acid.

501. Action of Concentrated Sulphuric Acid.

Cold, concentrated sulphuric acid converts some of the sugars into definite compounds, the body yielded by dextrose being $4C_6H_{12}O_6,SO_3$. This behaviour distinguishes dextrose from cane sugar, which is carbonised by concentrated sulphuric acid with great facility. A strong syrup of cane or milk sugar mixed with concentrated sulphuric acid is immediately decomposed with evolution of sulphur dioxide and other volatile products, and formation of a very bulky, black, carbonaceous mass.

ACTION OF DILUTE ACIDS ON SUGARS. INVERSION.

502. When an aqueous solution of cane sugar is heated with dilute sulphuric or hydrochloric acid, the solution increases in density, and the sugar loses its power of readily crystallising. This change in properties is attended by the assimilation of the elements of water, with formation of the mixture of sucro-dextrose

and sucro-lævulose known as inverted or invert sugar:—$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$. The rate of inversion depends mainly on the proportion of acid used, its chemical activity, and the temperature employed in the operation. Thus, dilute sulphuric and hydrochloric acids effect the inversion of cane sugar at the ordinary temperature after some time, and the change is very rapid at a temperature of 65° to 70° C. On the other hand, acetic, tartaric, citric, and sulphurous acids act very slowly at ordinary temperatures. Concentrated solutions of cane sugar are completely inverted with considerable difficulty.

503. The property of undergoing hydrolysis by heating with dilute acids is not limited to sucrose, being apparently common to all the saccharoses. In some cases two dissimilar glucoses result, while in others but one variety appears to be produced.

504. When a solution of cane sugar is converted by hydrolysis into one of lævulo-dextrose, the optical activity is changed from *right* to *left-handed*, or is "inverted." The term *inversion* is now applied generally to the process of hydrolysis of the saccharoses, whether or not the same optical change be produced.

The following table shows the products of the hydrolysis, or "inversion" of the principal saccharoses:—

SACCHAROSE, $C_{12}H_{22}O_{11}$.	RESULTANT GLUCOSES, $C_6H_{12}O_6$.
Cane sugar.	Sucro-dextrose and lævulose.
Milk sugar.	Sucro-dextrose and galactose.
Maltose.	Sucro-dextrose.
Melitose.	Dextrose and eucalyn.
Melezitose.	Dextrose.
Synanthrose.	Dextrose and a lævo-glucose.
Mycose.	Dextrose.

505. SUCROSE is most readily and certainly inverted by adding, to a solution containing not more than 25 grammes of the solid per 100 c.c., one-tenth of its bulk of fuming hydrochloric acid, and then heating the liquid to 70° C. for ten or fifteen minutes. Some operators prefer dilute sulphuric to hydrochloric acid, and heat the liquid to boiling for five or ten minutes. (See also par. 207.)

The inversion of sucrose by yeast-infusion is described in par. 563.

506. MILK SUGAR is less readily inverted than sucrose, being unaffected by boiling for ten minutes with two grammes of citric acid per 100 c.c. of the solution.

507. **Maltose** is inverted less readily than sucrose, boiling for five minutes with dilute sulphuric acid producing comparatively little change. Its inversion is best effected by adding 3 c.c. of concentrated sulphuric acid to each 100 c.c. of the solution, and heating the liquid in a water-bath for three or four hours. Any *dextrin* which may be present will be converted into dextrose simultaneously. According to Meissl, only 98·5 per cent. of maltose can be converted into dextrose by *boiling* with dilute sulphuric acid of the above strength, and this result is only attained under the most favourable conditions, as a point is ultimately reached at which the destruction of the ready-formed dextrose proceeds faster than its formation. Hence too long a treatment is objectionable.

508. In effecting the inversion of maltose and dextrin by dilute acid, it is very desirable to watch the progress of the operation by testing sample-portions of the liquid periodically. When two successive portions of the solution yield the same results on being appropriately tested, the reaction is complete. To facilitate the taking of the samples, the acidulated sugar-solution may be conveniently contained in a tapped separator (fig. 7, par. 86) furnished above with a cork and long glass tube, and immersed in boiling water. This arrangement prevents any charring of the sugar by concentration of the sulphuric acid on the sides of the vessel. Samples of the solution may be removed through the tap periodically and tested. When the polarimeter is used, the sample quantity can be returned to the bulk and the whole further heated, but when Fehling's solution or other chemical reagent is employed this is not practicable. In such cases, it is sometimes convenient to divide the original solution into a series of small quantities of 10 c.c. each, placed in test-tubes loosely corked. The test-tubes are surrounded by an india-rubber band, and immersed together in boiling water, one of them being removed from time to time for the contents to be tested.

H. T. Brown and Charles Graham condemn the use of increased pressure when an accurate conversion of maltose or dextrin to dextrose is desired, but C. O'Sullivan informs the author that the purest yield of dextrose is obtained by heating 30 grammes of the saccharine matter in 100 c.c. of water containing 1 c.c. of sulphuric acid, at a pressure of one additional atmosphere or less. Under these circumstances pure dextrose results after a treatment of twelve to twenty minutes.[1]

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[1] A suitable apparatus for heating such liquids under increased pressure consists of a soda-water bottle fitted with an india-rubber stopper through which passes a long glass tube, which is bent twice at right-angles and immersed to a depth of 30 inches in mercury contained in a long vertical glass

When the inverted solution of a sugar is to be decolorised by basic acetate of lead, or treated by Fehling's solution, the free acid contained in it should first be *nearly* neutralised by the addition of sodium carbonate.

509. By the prolonged action of dilute acid on sugars, the hydrolysis goes a step further, with formation of an unfermentable body of the formula $C_6H_{14}O_7$.

510. FERMENTATION OF SUGARS.

On reference to the tables (p. 189 *et seq.*) it will be seen that the three classes of sugars are distinguished from each other by their behaviour with ferments, the *saccharoids* being unfermentable, the *glucoses* directly fermentable, and the *saccharoses* capable of fermentation after inversion by yeast or dilute acids.

511. Action of Yeast.

The formation of alcohol and other products by the action of yeast on saccharine solutions has already been described (par. 165 *et seq.*).

As a certain time is required for the inversion of cane sugar or other saccharose by yeast, the glucoses usually ferment more readily and quickly than the saccharoses. Indeed, if the proportion of yeast be very small, the change of sucrose does not go beyond the formation of invert sugar. (See also par. 562 *et seq.*)

512. Detection of a Fermentable Sugar.

To recognise the presence of a fermentable sugar the substance should be dissolved in water in such proportion, or the liquid should be concentrated to such an extent, as to produce a solution containing from 5 to 15 per cent. of saccharine matter (a solution of cane sugar of a density of 1038·6 contains 10 grammes of the solid per 100 c.c.). The liquid is neutralised, if already acid, and then slightly acidulated with tartaric acid, and mixed with a little good yeast, previously washed with cold distilled water and free from starch. 5 c.c. of the liquid should then be introduced, by means of the cup, into the tube of a nitrometer filled with mercury, and kept at a temperature of 20° to 30° C. If a glucose be present, carbon dioxide will be evolved in a few hours, and will displace the mercury in the nitrometer. Cane sugar and other saccharoses require a longer time for fermentation to set in, but in the end their behaviour is the same.

tube or piece of narrow gas-pipe. The stopper should be carefully secured by wire. The soda-water bottle may be heated in a bath of paraffin or oil, or in a boiling saturated solution of sodium nitrate. This has a temperature corresponding to an additional atmosphere of pressure, so that no regulation is required.

It is always desirable to make a blank experiment, so as to ascertain positively that the yeast does not itself yield any notable quantity of carbonic acid under the conditions of the experiment.

A negative result with yeast does not absolutely prove the absence of a fermentable sugar, as very small quantities of thymol, salicylic acid, and other antiseptics wholly prevent the alcoholic fermentation.

513. DETERMINATION OF SUGARS BY FERMENTATION.

The foregoing process may readily be made roughly *quantitative*, but if that be desired it is better to operate in an apparatus such as is employed for the analysis of carbonates, and determine the dry carbon dioxide from the loss of weight undergone by the apparatus. The fermentation is usually practically complete in forty-eight hours, but should be continued as long as any notable quantity of gas continues to be evolved. The weight of carbon dioxide evolved, multiplied by 2·0454, gives that of the glucose fermented, which figure multiplied by 0·95 gives the corresponding weight of cane sugar or other saccharose.

514. Instead of measuring or weighing the carbon dioxide produced it is in some respects preferable to determine the *alcohol* formed. The process is conducted as already described, but it is not desirable to employ less than 50 or 100 c.c. of the solution, which should by preference have a concentration of 12 to 16 per cent.; 0·5 gramme of pressed fresh yeast is sufficient in most cases, especially if a little yeast-ash be added, but it is desirable to add a little more yeast at the end of the action to ensure that no further fermentation can be induced. The liquid should be kept at a temperature of 20° to 25° C. for two or three days, after which the liquid is distilled to about one-third, the distillate weighed, and the alcohol contained in it ascertained from the density (par. 163, *b*). The weight of alcohol thus found when multiplied by 2·02 gives the glucose, or by 1·96 the cane sugar from which it was derived.

Some operators prefer to employ a large quantity of yeast, such as 10 or even 20 grammes.[1] In such cases, it is very desirable to conduct a blank experiment with the same quantity of yeast and water, side by side with the test of the saccharine liquid, and to deduct the alcohol found in the former case from that obtained in the latter, before calculating to the equivalent of sugar. A still better plan, perhaps, is to ferment a solution of cane or invert sugar, of known strength, side by side with the samples, when the amounts of sugar in the two liquids will bear to each other the same proportion as the amounts of alcohol produced by their distillation.

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[1] Dr James Bell recommends the use of 100 grains of sugar in ½ per cent. solution, which is fermented with 200 grains of yeast. There seems to be no advantage in using so dilute a saccharine liquid.

515. Another method which has been suggested for estimating sugar from the results of its fermentation by yeast consists in noting the "gravity lost" in the process. That is, the density of the original saccharine solution is observed and compared with that of the fermented liquid, after filtering, washing the residue, boiling off the alcohol, and making up the solution to its original volume. The difference is the "gravity lost" by the fermentation. The "spirit-indication" corresponding to the value thus found is ascertained by reference to the table on page 99, and this figure subtracted from 1000 gives the density of the dilute alcohol produced by the fermentation. The strength of this can be ascertained by reference to the tables in par. 156, and the weight so arrived at can be calculated into its equivalent of cane sugar or maltose by the factor $\frac{100}{51} = 1{\cdot}96$, or into glucose by the factor $\frac{100}{49{\cdot}5} = 2{\cdot}02$. The glucose may also be deduced by calculating 0·219 per cent. for each degree of gravity lost.

It is evident that the last described method can be advantageously employed as a check on the distillation process.

516. Instead of estimating the sugar from the density of the solution before and after fermentation, equal volumes of the original and the filtered fermented liquids may be evaporated to dryness, and the quantity of sugar deduced from the loss of weight. An addition of 5 per cent. to the amount of sugar thus found should be made as a correction for the succinic acid and glycerin which are produced by the fermentation and remain in the residue from the fermented liquid. When the quantity of sugar is small, this method is preferable to an estimate based on the gravity lost.

In determining sugar by fermentation with yeast it is desirable to add to the solution a little yeast-ash, or phosphate of sodium and nitrate of potassium, so as to furnish the yeast with the inorganic elements requisite for its nutrition.

The determination of sugar by fermentation with yeast is occasionally very valuable, and when the process is carefully conducted the results are fairly accurate.

517. Lactous Fermentation.

Under the influence of certain organisms or ferments contained in decomposing albuminous matters, many of the sugars are converted into lactic acid, in accordance with the following equation:— $C_6H_{12}O_6 = 2C_3H_6O_3$. The action soon comes to an end in practice through the retarding influence of the lactic acid produced, but if this be kept constantly neutralised the fermentation proceeds until the whole of the sugar is transformed. This usually occurs in two or three weeks, but if the experiment be further prolonged the lactic acid first produced is decomposed, with evolution of hydrogen and carbon dioxide and formation of butyric acid.

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + H_2.$$

518. In practice, the lactous fermentation is most conveniently excited by putrid cheese, chalk or magnesia being added to the liquid to neutralise the lactic acid as fast as it is formed. The following are suitable conditions for conducting the process, and hence for ascertaining whether a particular sugar is capable of undergoing the lactous fermentation:—A solution of the sugar in 10 to 15 parts of water is treated with some whiting or prepared chalk, and some old decayed cheese added. The mixture is maintained at a temperature of 30° to 35° C, and stirred from time to time. After standing ten or twelve days, an equal measure of boiling water is added, together with sufficient lime to render the reaction distinctly alkaline to litmus. The liquid is then boiled and filtered through calico. The filtrate is concentrated by evaporation till it deposits crystals of calcium lactate on cooling. These are removed, pressed, and decomposed by dilute sulphuric acid, the calcium sulphate filtered off, and the filtrate saturated with zinc carbonate. On concentrating the resultant solution zinc lactate can be obtained in crystals, which can be identified by their form and other characters.

The behaviour of the various kinds of sugar with cheese and chalk is described in the tables on page 189 *et seq.*

ACTION OF ALKALIES ON SUGARS.

519. Cane sugar and the other sugars of the formula $C_{12}H_{22}O_{11}$ are not attacked by dilute caustic alkalies in the cold, and only slowly on heating, but they are decomposed by boiling with concentrated alkaline solutions; and when fused with caustic potash yield oxalate and acetate of potassium and other products.

520. Cane and milk sugars act as weak acids, and form definite compounds with the alkalies and other bases (see par. 559).

521. Alkalies decompose glucoses much more readily than saccharoses, though metallic derivatives of an unstable character are in some instances obtainable. Thus sodium dextrosate, $C_6H_{11}NaO_6$, is produced as a bulky white precipitate on adding sodium ethylate to a solution of dextrose in absolute alcohol. It is extremely hygroscopic, agglutinating on exposure to the air, and apparently decomposing into caustic soda and dextrose.

522. When heated with a strong solution of caustic soda, the

glucoses form brown liquids. Baryta and lime act somewhat similarly, the rapidity of the change depending on the temperature and concentration of the solution. If a dilute solution of dextrose saturated with lime be allowed to stand in the cold, the coloration will not exceed a pale yellow, but the alkalinity of the liquid will be found to have somewhat diminished, and the optical activity will be greatly reduced. On saturating the liquid with carbonic acid and filtering, a solution is obtained which is optically inactive, but of which the cupric oxide reducing power does not differ much from that of the original dextrose. The liquid is found to contain the lime compound of a substance called saccharin, together with another body to be presently described.

523. SACCHARIN, as isolated by Peligot from the products of the action of lime on dextrose, is a body crystallising in rhombic prisms, melting at 160°, and volatile almost without decomposition. It is dextro-rotatory, the value for S_D being $+92°\cdot8$. Saccharin is not capable of inversion or fermentation, and does not reduce Fehling's solution. It decomposes carbonates when boiled with them, forming saccharinates, from which the free acid cannot be obtained, as it splits up into water and saccharin. Peligot considers saccharin to be isomeric with cane sugar, but Scheibler gives it the formula $C_6H_{10}O_5$, and regards it as the anhydride of saccharinic acid, $C_6H_{12}O_6$, which forms a series of very soluble salts, those of potassium and ammonium being crystallisable.

524. Cuisinier has extended the knowledge of saccharin, and shown that it is produced by the action of lime on lævulose as well as dextrose. He suggests that it should be called glucosaccharin to distinguish it from the isomeric body he has obtained by the action of lime on maltose (which has a rotatory power of $+63°$), and from the meta-saccharin obtained by Kiliani from milk sugar ($S_D = -48\cdot4$).

525. Besides saccharin, the action of lime on glucoses results in the formation of an optically active, non-fermentable body, neutral to litmus and forming a non-saturated compound with lime. This substance easily alters in presence of alkalies, giving rise to brown matters with reduction of the alkalinity of the liquid. It is very easily oxidisable, its alkaline solution taking oxygen from the air and readily reducing Fehling's solution. It is to the formation of this body by the action of alkalies that the reaction of reducing sugars with Fehling's solution is probably due, the saccharin simultaneously formed having no such reducing power. Thus, on adding a glucose to Fehling's solution the free alkali quickly decomposes the sugar with formation of saccharin, which combines with a portion of the alkali, also producing the neutral body, which is oxidised

by the cupric oxide with formation of another acid which neutralises more of the alkali. If the addition of glucose be continued after all the copper present is reduced, another reaction sets in, and brown products result. From observations on the reduction of the alkalinity of the lime-glucose solution, as compared with its cupric oxide reducing power, Cuisinier believes the glucoses to be compounds of saccharin with the neutral oxidisable body. This he regards as a polyatomic alcohol, the glucoses being saccharinic or isosaccharinic ethers of this body.

526. When dextrose or lactose is heated with strong aqueous *ammonia* to 150° C., under pressure, a nitrogenous substance is produced, precipitable by alcohol in tenacious threads, which form with tannin an insoluble, non-putrescible compound.[1]

REACTIONS OF THE SUGARS AS REDUCING AGENTS.

527. Many sugars, including the different species of glucose, possess considerable activity as reducing agents, while in the case of other kinds, as cane sugar, the reducing power is comparatively feebly marked.

528. In hot alkaline solution, the glucoses reduce picric acid to picramic acid, indigotin to white indigo, and change ferricyanides to ferrocyanides.[2] Bismuth, mercury, silver, platinum, and gold are reduced to metal, and ferric and cupric salts to ferrous and cuprous compounds respectively.

The reducing properties of sugars are best manifested and measured by their reaction on alkaline solutions of cupric and mercuric salts, and hence the processes in which these are employed are the only ones of the kind which require to be described in detail.

529. Reaction of Sugars with Cupric Salts in Alkaline Solution.

If a solution of cupric sulphate be mixed with a sufficient quantity of a saccharine liquid, no precipitate of hydrated cupric oxide, CuO,H_2O, is produced on addition of caustic potash or soda. The liquid acquires a deep blue colour, but remains perfectly clear. On raising the fluid to the boiling point, no visible change occurs

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[1] $$\underset{\text{Glucose.}}{C_6H_{12}O_6} + 2NH_3 = \underset{\text{Body allied to gelatin.}}{C_6H_{10}N_2O_2} + 4H_2O.$$

On the other hand, by the action of dilute acids, gelatin forms, among other products, glycocine and sugars resembling the glucoses.

[2] The last reaction has been made the basis of a process of determining glucose (Gentèle, *Jour. Chem. Soc.*, xxxii. 226; xxxiv. 246; xxxvi. 180), of which O'Sullivan speaks favourably.

if the liquid contained cane sugar only, but, if any species of glucose be present, a yellow precipitate of hydrated cuprous oxide is produced, which quickly turns to anhydrous Cu_2O and acquires an orange-red colour. If the glucose be present in excess the blue colour of the solution entirely disappears. Instead of relying on the saccharine matter for the prevention of the precipitation of the blue cupric hydrate by the alkali it is far better to employ tartaric acid or a tartrate, as in Fehling's solution.

The reducing action of certain varieties of sugar on alkaline solutions of copper has been applied by different chemists in an almost infinite variety of ways, the precipitated cuprous oxide being weighed as such by several, by others converted into metallic copper or cupric oxide, and by others redissolved and estimated volumetrically. Some operators make the original process a volumetric one. The great majority of these modified processes are merely of historical interest and require no detailed description.[1]

530. Fehling's Copper Solution.

The alkaline solution of copper most commonly employed for the determination of sugars is that known as Fehling's, which is essentially a solution of the double tartrate of copper and sodium containing a considerable quantity of caustic soda. It is best prepared in the following manner:—34·64 grammes weight of pure crystallised sulphate of copper (free from iron and moisture) is dissolved in distilled water, and the solution diluted to 500 c.c. 70 grammes of caustic soda of good quality (not less than 97% NaHO) and 180 grammes of recrystallised Rochelle salt (potassium sodium tartrate)[1] are dissolved in about 400 c.c. of water and the solution diluted to 500 c.c. Fehling's solution is prepared by carefully adding the cupric sulphate solution to an equal measure of the alkaline tartrate solution. It may be kept ready-mixed, but should in that case be carefully protected from air and light, as it is apt to undergo some obscure change which renders its indications unreliable. Hence, before using Fehling's solution it is desirable to ascertain its condition, by diluting a quantity with an equal measure of water and heating the liquid to boiling for a few minutes. It ought to remain perfectly clear. Old Fehling's solution may sometimes be rendered fit for use by adding more soda, but its quantitative indications should not be relied on. It is preferable to keep the cupric and tartrate solutions separate, and mix them in equal measures at frequent intervals.

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[1] The reduction of copper solutions by glucose appears first to have been utilised as a qualitative test by Trömmer. Barreswil first employed the reaction for quantitative purposes. Frommherz suggested the employment of a citrate to keep the cupric oxide in solution. Modifications of the ordinary alkaline tartrate solution have been devised by Barreswil, Poggiale, Rosenthal, Chevalier, Boussingault, Reveil, Fehling, Strohl, Monier, Viollette, Magneshahens, Lowenthal, Joulie, Possoz, &c. Loewe employed glycerin instead of a tartrate. Various treatments of the precipitated cuprous oxide have been proposed by the following chemists:—Mohr dissolves the oxide in hydrochloric acid and titrates with permanganate. Brunner dissolves in an acid solution of ferric chloride, and estimates the reduced iron by bichromate or permanganate. Champion and Pellet dissolve the precipitate in hydrochloric acid and chlorate of potassium, boil off free chlorine, and titrate the liquid with stannous chloride. Girard and Soxhlet reduce the cuprous oxide in hydrogen and weigh the metallic copper. Muter dries the cuprous oxide at 100° C., and weighs it as Cu_2O. O'Sullivan and other operators ignite the precipitate strongly and weigh as CuO. Ferdinard-Jean dissolves the cuprous oxide in hydrochloric acid, and weighs the metallic silver precipitated on adding ammoniacal silver nitrate. Maumené uses an excess of copper solution, filters, adds ammonia to the filtrate, and estimates the residual copper by titration with sodium sulphide, for which Perrot substitutes potassium cyanide. Lastly, Pavy adds ammonia to the alkaline cupric solution and runs in the sugar solution till the hot liquid is decolorised.

531. For the *detection of a reducing sugar* in clear, colourless solution, all that is necessary is to neutralise any free acid and heat the liquid to the boiling point with twice its measure of Fehling's solution. If a yellow or orange-red turbidity or precipitate of cuprous oxide be produced, a reducing sugar, or some substance giving a similar reaction, is present.[2] The glucoses, maltose, and milk sugar reduce the copper solution with facility, but cane sugar gives no reaction till after "inversion" by heating with acid (par. 505).[3]

532. If a saccharine liquid be much coloured it is difficult or impossible properly to recognise the reaction with Fehling's solution. Coloration of the liquid is still more objectionable if the sugar is to be quantitatively determined, in particular by the volu-

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[1] Much of the Rochelle salt of commerce is very impure. It is safest to prepare it by dissolving commercial cream of tartar in hot water, adding carbonate of sodium till the liquid remains slightly alkaline after boiling, filtering from the precipitated calcium carbonate, and crystallising the Rochelle salt from the clear liquid. Many chemists employ 173 grammes of Rochelle salt, instead of 180 as recommended in the test, but the additional quantity renders the solution more permanent.

[2] The action of reducing sugars on Fehling's solution is not precisely known, but among the products are—1. Acetic and formic acids. 2. Certain non-volatile acids, especially tartronic; an acid forming uncrystallisable salts; and an acid decomposed with formation of humus-like products on heating its alkaline solution. 3. A gum-like substance.

[3] The behaviour of the various species of sugar with Fehling's solution is described in the tables on page 189 *et seq.*, and that of other organic bodies in the section on "Cupric Tartrate."

metric process. In such cases the sugar solution must be clarified by one of the methods employed for the preparation of a solution for the polarimeter (see page 200), but it must be borne in mind that if lead has been employed it must be *completely* removed from the solution, or the results of the Fehling's test will be worthless. To prepare the clarified sugar solution containing lead for the copper test, a quantity of it, judged to contain from 2 to 5 grammes of glucose, is accurately measured and placed in a 100 c.c. flask. A strong solution of sulphurous acid is next added, until the lead is completely precipitated, when a little washed alumina is added, the fluid diluted to the mark with water, agitated, and filtered. The clear filtrate is then ready for addition to the cupric solution as described below.

533. *The inversion of cane sugar* to render it determinable by copper solution may be affected as described in par. 477, taking care that the liquid is first clarified if necessary, and then freed from lead as described above. By operating in this manner a very satisfactory solution is obtained, and excessive colour is avoided. The acid liquid must be rendered neutral by carbonate of sodium before adding it to the Fehling's solution.

534. Fehling's solution has been very widely used for the *determination of reducing sugars*, and has been employed in various ways. Broadly speaking, it may be used volumetrically or gravimetrically. Both methods are capable of giving useful approximate results, but if any high degree of accuracy be sought, it is essential that certain conditions of manipulation be strictly adhered to.

As a good approximate estimation of the amount of reducing sugar present in a liquid is often all that is requisite, it will be convenient to give methods by which such results can be readily obtained, and subsequently to describe the conditions which must be observed if a higher degree of accuracy be desired.

535. Volumetric Determination of Reducing Sugars by Fehling's Solution.

The saccharine solution, prepared as already described, and containing from 0·5 to 1·0 gramme of sugar per 100 c.c., is placed in a burette. Exactly 10 c.c. of the Fehling's solution are measured into a wide test-tube or small flask supported vertically by a clip. 30 c.c. of water are added, and a few fragments of tobacco-pipe stem dropped in to prevent bumping. The liquid is heated to boiling by applying a small flame, and the sugar solution run in, 2 c.c. at a time, boiling between each addition. When the blue colour of the liquid has nearly disappeared, the sugar solution should be added more cautiously, but it is desirable to effect the titration as rapidly as possible. The end of the reaction is reached when, on removing the flame and allowing the cuprous oxide to settle, the supernatant fluid appears colourless, or faintly yellow, when viewed against a white surface. If any doubt be felt as to the termination of the reaction, a few drops of the liquid may be filtered through a small filter into a mixture of acetic acid and dilute potassium ferrocyanide, contained in a porcelain crucible or placed on a white plate. If copper be still present in the liquid, more or less brown coloration will be observed.

The results obtained by using Fehling's solution volumetrically are not generally so accurate as those of the gravimetric method. The operation should be *quickly* conducted.[1]

536. The following are the weights of the principal kinds of sugar which, it is generally assumed, will reduce 10 c.c. of Fehling's solution prepared as described in par. 530. Soxhlet's figures are given in par. 545.

10 c.c. Fehling solution = ·0500 gramme of dextrose, lævulose, or invert sugar.
10 c.c. ,, ,, = ·0475 ,, cane sugar (after inversion).
10 c.c. ,, ,, = ·0678 ,, milk sugar (lactose).
10 c.c. ,, ,, = ·0807 [2] ,, malt sugar (maltose).

In all cases in which Fehling's solution is to be used volumetrically, its true oxidising power under the conditions of the experiment should be ascertained by actual trial. ·0475 gramme of dry cane sugar, after being inverted as described in par. 477, and the solution neutralised, should exactly decolorise 10 c.c. of Fehling's solution.

537. Gravimetric Determination of Reducing Sugars by Fehling's Solution.

25 to 30 c.c. of Fehling's solution, prepared as described in par. 530, should be placed in a beaker of about 5 or 6 ounces' capacity, and diluted with 50 c.c. of boiling well-boiled water. The beaker is placed in a larger one in which water is kept constantly boiling. At the end of six or seven minutes (the liquid being still perfectly clear) a known weight or measure of the glucose-holding liquid, previously clarified, inverted, and neutralised if necessary (see par 533), is added to the hot Fehling's solution, and the water kept boiling in the outer beaker for twelve or fourteen minutes. If the blue colour of the solution be completely destroyed within the first few minutes it can be restored by quickly adding more of the Fehling's solution, but it is much safer to commence the assay

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[1] In presence of much albuminous or other impurity in the sugar solution, the cuprous oxide refuses to settle, and remains suspended in a fine state of division, rendering the whole liquid muddy. Efficient previous clarification will always prevent this inconvenience and render unnecessary the filtration of a few drops of the turbid liquid, with subsequent testing for copper, by acidulating and adding sulphuretted hydrogen or potassium ferrocyanide.

[2] See par. 612.

again, using a smaller amount of the saccharine liquid. After twelve or fourteen minutes the precipitated cuprous oxide is rapidly filtered, washed with boiling well-boiled water, dried, and ignited in porcelain. Strong ignition for five or six minutes in an open crucible ensures the conversion of the red precipitate into the black cupric oxide (CuO), and treatment with nitric acid is hence rarely necessary. The oxide of copper must be cooled under a dessicator and weighed as rapidly as possible, as it is extremely hygroscopic.

Although the above method is very satisfactory, some chemists prefer to weigh the cuprous oxide direct, or to redissolve the precipitate, either before or after ignition, and deposit the metallic copper on the inside of a platinum crucible by electrolysis.

The details of manipulation just given are those recommended by O'Sullivan (*Jour. Chem. Soc.*, xxx. 131) for the estimation of maltose in beer-worts, &c. The determination of milk sugar by Fehling's solution requires certain modifications to insure accuracy, and is best effected as described in par. 656.

538. The following factors may be employed for calculating the weight of copper or oxide of copper obtained to the corresponding quantities of the principal kinds of sugar. (See also par. 545).

	Glucose, $C_6H_{12}O_6$.	Cane Sugar, $C_{12}H_{22}O_{11}$ (after inversion).	Milk Sugar, $C_{12}H_{22}O_{11}$.	Malt Sugar, $C_{12}H_{22}O_{11}$.
Cu . .	·5634	·5395	·7707	·9089
Cu_2O . .	·5042	·4790	·6843	·8132
CuO . .	·4535	·4308	·6153	·7314

Thus, if a solution of 0·1 gramme of a sample of cane sugar has been inverted and precipitated as above described, and the resultant CuO weighs 0·198 gramme, then the total quantity of sugar (expressed as cane sugar) is—

$$0{\cdot}198 \times {\cdot}4308 = {\cdot}085298 = 85{\cdot}3 \text{ per cent.}$$

539. TITRATION BY PAVY'S AMMONIACAL CUPRIC SOLUTION.

This modification of the ordinary mode of using Fehling's solution for the estimation of reducing sugars is based on the fact that in presence of a sufficient excess of ammonia the cuprous oxide is not precipitated, but forms a *colourless* solution, so that the end of the reaction is indicated by the decolorisation of the blue liquid. As the ammoniacal cuprous solution is extremely oxidisable, the blue colour being restored by oxidation, it is necessary to avoid access of air. This is best done by attaching the nose of the Mohr's burette containing the sugar solution to a tube passing through the india-rubber stopper of a flask containing the copper solution. A second tube conveys the steam and ammoniacal gas into a flask of cold water. It is desirable to allow the end of the tube to dip into a little mercury placed at the bottom of the water, so as to prevent any tendency to "suck back." A still better arrangement is to pass (by a third tube) a slow current of hydrogen or coal-gas through the flask containing the boiling copper solution.

To prepare the ammoniacal solution, 120 c.c. of the ordinary Fehling's solution (see par. 530) should be mixed with 300 c.c. of strong ammonia (sp. gr. ·880), and with 400 c.c. of caustic soda solution of 1·14 sp. gr. (=12 per cent.). The mixture is then made up to 1 litre. 100 c.c. measure of this solution has the same oxidising power on glucose as 10 c.c. of the ordinary Fehling's solution, that is, it corresponds to ·050 gramme.

In carrying out the process, 100 c.c. of the above solution are placed in the flask, a few fragments of pumice or tobacco-pipe added, the tubes and burette adjusted, and the liquid brought to ebullition. The sugar solution is then gradually run in from the burette, the boiling being continued regularly. The process is at an end when the blue colour of the liquid is wholly destroyed. The end-reaction is very sharply marked, but the reduction occurs more slowly than with the ordinary Fehling's solution. The process is often a very useful one, especially for the rapid assay of impure saccharine liquids such as beer-worts.

Pavy's solution is said to possess a different oxidising power on maltose (see par. 536) and lactose from that exerted by Fehling's test. Its reaction on invert sugar is, under the above-described conditions, only five-sixths of that exerted by Fehling's solution. Hence 120 c.c. of the latter are employed in making the ammoniacal solution, instead of 100, as would be the case if they were strictly equivalent.

O. Hehner has shown (*Analyst*, vi. 218) that the presence of a varying proportion of salts, such as alkaline tartrates and carbonates, gravely affects the accuracy of the indications obtained by Pavy's solution.

540. Reaction of Sugars with Solutions of Mercury.

Several methods have been described of determining glucoses by their reducing action on mercuric solutions, an alkaline solution of potassio-mercuric cyanide being recommended by Knapp; an alkaline solution of potassium mercuric iodide by Sachsse; and a solution of mercuric acetate by Hager. The first two of these reagents have valuable qualities.

541. KNAPP'S MERCURIC SOLUTION is strongly recommended by

Müller and Hager for determining the glucose in *diabetic urine*, the process being conducted in the following manner:—

A standard solution is prepared by dissolving 10 grammes of pure dry mercuric cyanide in water, adding 100 c.c. of caustic soda solution of 1·145 sp. gr., and diluting the liquid to 1000 c.c. 10 c.c. of this liquid are reduced by 0·025 grammes of diabetic sugar (dextrose). 10 c.c. of the standard solution are diluted with 20 to 30 c.c. of water, and the liquid heated to the point of boiling. The urine, previously diluted with water to five or ten times its volume, is then run in from a burette till the whole of the mercury is precipitated. When the precipitate has settled, a drop of the supernatant liquid, which has a more or less yellow colour, is transferred by a glass tube to a piece of *thin*, *pure white*, Swedish filter paper. The paper is held over a bottle containing fuming hydrochloric acid, and then over a vessel containing strong solution of sulphuretted hydrogen. The slightest trace of mercury is shown by the production of a light-brown or yellow stain. It is desirable to compare a drop of the original liquid side by side which has been subjected to the treatment with the acid gases. By thus working, the slightest trace of mercury remaining in the liquid may be detected. Of course it is desirable to repeat the titration. Knapp's solution undergoes no change on keeping.

For the analysis of ordinary glucose solutions, 40 c.c. of Knapp's reagent should be diluted to 100 c.c. and the sugar solution (not stronger than ½ per cent.) run in *as quickly as possible*.

An alkaline solution of mercuric cyanide has been employed by H. W. Wiley for oxidising and destroying dextrose and maltose while leaving dextrin unchanged (see par. 701).

542. Sachsse's Mercuric Solution is prepared by dissolving 18 grammes of pure dry mercuric iodide in a solution of 25 grammes of potassium iodide. To this a solution of 80 grammes of caustic potash is added, and the solution diluted to 1 litre. 40 c.c. of this solution are boiled in a basin, and a standard solution of the sugar gradually added. The end of the reaction is attained when a drop of the supernatant liquid ceases to give a brown colour with a drop of a very alkaline solution of stannous chloride. The end of the reaction is well defined, and the results are accurate when pure dextrose or inverted sugar is worked with, though differing with each.[1] In presence of cane sugar the results are quite erroneous. By reducing the proportion of caustic potash from 80 grammes to 10 grammes per litre, Heinrich finds that glucose may be accurately determined in presence of very varying amounts of cane sugar.

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[1] 40 c.c. of Sachsse's solution is reduced by 0·1342 gramme of dextrose, or 0·1072 of invert sugar.

543. The solutions of Knapp and Sachsse cannot advantageously replace that of Fehling for ordinary purposes, but occasionally they are capable of being applied with great advantage. This is owing to the fact that they are unequally affected by the different kinds of reducing sugars, and even the two mercurial solutions exhibit essential differences in this respect. The subject has been recently investigated by Soxhlet (*Jour. Prac. Chem.*, [2] xxi. 227; and *Jour. Chem. Soc.*, xxxviii. 758), who gives the following table. The numbers must not be interpreted too rigidly, but regarded as roughly comparative rather than absolute determinations of reducing power.

	Fehling.	Knapp.	Sachsse.
Dextrose, ...	100	100	100
Invert sugar, ...	96·2	99·0 (100 ?)	124·5
Lævulose, ...	92·4	102·2 (100 ?)	148·6
Milk sugar, ...	70·3	64·9	70·9
Lacto-glucose, ...	93·2	83·0	74·8
Inverted-milk sugar, . .	96·2	90·0	85·5
Maltose, ...	61·0	63·8	65·0

Some of Soxhlet's results are not accepted as accurate (see par. 545), and further investigation of the subject is much wanted. His observations are very suggestive of possible means of differentiating various sugars.

544. **Influence of Variable Conditions on the Reducing Power of Sugar Solutions.**—In all experiments on the reducing power of sugar on metallic solutions, it is important to operate as far as possible under constant conditions. Apparently unimportant variations, as time occupied in the experiment, amount of free alkali, presence of excess of the metallic solution, concentration of the liquid, and other conditions liable to change with every experiment, are all factors more or less concerned in the results obtained, and rigidly accurate results thus become impossible in many cases likely to occur in the practical analysis of saccharine liquids. The variations due to some of the above causes have been studied by Soxhlet (*Jour. Prac. Chem.*, [2] xxi. 227–317), a very full abstract of whose original paper has been published in English by C. H. Hutchinson (*Pharm. Jour.*, [3] xi. 721). Soxhlet finds that the reducing power of sugar for alkaline copper solutions is only constant under exactly the same conditions, and that if the same amount of sugar act in one case on an amount of copper solution which it is just able to reduce, and in another on an excessive quantity, the reducing

equivalent will in the first case be found to be considerably less than in the second. Evidently, therefore, if a solution of sugar be added by small quantities at a time to a copper solution, as in an ordinary volumetric estimation, the amount of reduction effected by the first quantities added will be greater than that produced by the last. To avoid the error due to this cause Soxhlet employs the sugar and copper solutions in the exact proportions necessary for their mutual reaction, ascertaining the volumes requisite by a series of approximating experiments.[1]

545. The following results were obtained by Soxhlet by operating in the manner described. The sugar solutions contained 1 gramme of the solid in 100 c.c. The figures represent the weight of the sugars in grammes required for the reduction of 100 c.c. of Fehling's solution, used undiluted or mixed with one, two, three, or four measures of water.

Kind of Sugar.	Time of Heating in Minutes.	Weight of Sugar oxidised by 100 c.c. of Fehling's Solution.				
		Undiluted.	Equal Bulk of Water.	Two Measures Water.	Three Measures Water.	Four Measures Water.
Dextrose (anhydrous)	2	·4750	·4825	·4880	·4920	·4940
Invert sugar .	2	·4940	·5030	·5090	·5140	·5150
Lævulose (calculated)	2	·5130	·5235	·5300	·5360	·5260
Milk sugar (dried at 100°)	6	·676	Unaffected by dilution.			·676
Lacto-glucose (dried at 100°)	2	·511	...	...	...	·533
Maltose . .	3 to 4	·778	...	...	...	·740

It will be seen from Soxhlet's results that dilution of the Fehling's solution very sensibly affects the reducing power exerted by the sugar. Thus one equivalent of invert sugar in 1 per cent. solution reduces 10·1 equivalents of CuO when the undiluted cupric solution is employed, but 9·7 equivalents only when Fehling's solution is diluted with four measures of water. It will also be observed that Soxhlet's results show a slight but very sensible difference between the reducing power of dextrose and of invert sugar, and this difference becomes more marked when the reducing power of lævulose is calculated therefrom.[1] This difference, if a real one, is of an exceedingly important nature, as it is calculated to vitiate very many of the analyses of saccharine matters on record. It is therefore greatly to be regretted that Soxhlet's conclusions are very seriously diminished in value by the questionable method adopted by him for effecting inversion.[2]

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[1] These were made by adding to a carefully measured quantity of Fehling's solution (prepared fresh daily), at the boiling point, a certain amount of a one per cent. or one-half per cent. solution of the sugar. The reaction was allowed to continue for a specified time, when the liquid was passed through a plaited filter, and a portion of the filtrate acidulated with acetic acid, and tested with potassium ferrocyanide. If a reddish-brown coloration or precipitate resulted, the experiment was repeated, a somewhat larger quantity of sugar solution being employed, and so on until a measure of sugar solution was found that would exactly suffice for the decomposition of the copper solution, while if 0·1 c.c. less of sugar solution were employed a sensible quantity of copper was found in the filtrate. Hence the volume of sugar solution required was ascertained to within 0·1 c.c.

The same objection applies to Soxhlet's experiments on the reducing power of invert sugar on the mercurial solutions of Knapp and Sachsse (see par. 540). In these cases, also, he found that the reducing equivalent was notably influenced by the concentration of the solution and the proportion of alkali present, and that any other variation in the conditions of working was likewise liable to influence the results.

546. RECOGNITION OF THE PRINCIPAL KINDS OF SUGAR.

When a sugar has been isolated in a condition of tolerable purity, it may be recognised by the special characters described in the tables on page 189 *et seq.*, with the aid of the additional details of manipulation given in the subsequent sections.

547. The detection or identification of a sugar by its reactions is greatly simplified by applying the tests in a systematic manner, and the following method of examination may be of service for distinguishing qualitatively between the more common species of sugar. For reasons of practical convenience the reactions of dextrin are also given.

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[1] According to Allihn the reducing powers of lævulose and dextrose are identical, if the heating with Fehling's solution be continued for half an hour.

[2] This was done by dissolving 9·5 grammes of purified cane sugar in 700 c.c. of water, adding 100 c.c. of one-fifth normal hydrochloric acid, and heating on the water-bath for thirty minutes. The solution was then exactly neutralised by caustic soda, and diluted with water to 1000 c.c. Soxhlet found that ·5 gramme (= ·475 of cane sugar) of inverted sugar so obtained reduced 101·2 c.c. of undiluted Fehling's solution, while with more prolonged heating with the same amount of acid the product reduced 100·5 c.c. of copper solution, and this was further reduced to 100·2 when 300 c.c. measure of the standard acid was employed, and the heating continued for ninety minutes.

	Dextrose $C_6H_{12}O_6$.	Lævulose $C_6H_{12}O_6$.	Milk Sugar $C_{12}H_{22}O_{11}+H_2O$.	Maltose $C_{12}H_{22}O_{11}+H_2O$.	Cane Sugar $C_{12}H_{22}O_{11}$.	Dextrin $C_6H_{10}O_5$.
1. Moisten the solid sugar with water, and stir in the cold with concentrated sulphuric acid (1·845 sp. gr.).	Not affected when pure.	Not affected when pure.	Not affected.	Slightly reddish or brownish, gradually turning darker.	Charred.	Not affected.
2. Triturate the solid sugar with caustic soda, or boil it with a 3 per cent. caustic soda solution for one minute.	Deep brown coloration.	Deep brown coloration.	Not affected.	Slightly discoloured.	Not affected.	Not affected.
3. To the neutral aqueous solution add a few drops of Fehling's copper solution, and heat to boiling for a few minutes.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	No change.	No change.
4. Heat the solution to boiling for half an hour with $\frac{1}{20}$th of its bulk of strong sulphuric acid, neutralise with soda, and heat to boiling with Fehling's solution for a few minutes.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.
5. To a few drops of Fehling's solution add caustic soda and ammonia, heat to boiling, and add the saccharine solution drop by drop, keeping the liquid boiling (Pavy's test).	Liquid decolorised.	Liquid decolorised.	Liquid decolorised.	Liquid decolorised.	No change.	No change.
6. Boil the solution for two minutes with 1 c.c. of a liquid containing 4 per cent. of cupric acetate and 1 per cent. of acetic acid ($C_2H_4O_2$).	Red precipitate of Cu_2O.	Red precipitate of Cu_2O.	No change.	No change.	No change.	No change.
7. Observe the solution in the polarimeter.	Dextro-rotatory.	Lævo-rotatory.	Dextro-rotatory.	Dextro-rotatory.	Dextro-rotatory.	Dextro-rotatory.
8. Heat solution with dilute acid as in test 4, and observe again in polarimeter.	Dextro-rotatory power *unchanged.*	Lævo-rotatory power *unchanged.*	Dextro-rotatory power *increased.*	Dextro-rotatory power *diminished.*	Dextro-rotatory power *changed to lævo-rotatory.*	Dextro-rotatory power *diminished.*
9. Treat the sugar with moderately concentrated nitric acid, and study the products of the oxidation as in par. 496.	Saccharic acid.	Saccharic acid.	*Mucic,* saccharic and oxalic acids.	Saccharic and oxalic acids.	Saccharic and oxalic acids.	Oxalic acid.

548. From an inspection of the table, it appears that all the substances referred to therein are optically active. Hence it is not possible to have an inactive solution containing a notable quantity of one of the above sugars. If lævulose were present together with a certain proportion of one of the other sugars, the solution might exhibit no rotation at first, but would do so on heating, owing to the reduced optical activity of lævulose in hot liquids.

Lævulose always occurs in practice in presence of more or less dextrose, and in such cases is best detected by the change in the optical activity of the solution on heating. Other distinctions between lævulose and dextrose will be found in par. 670.

The presence of a *glucose* of some sort is indicated by the behaviour of the sugar with tests 2 and 8.

Milk Sugar is only met with in products derived from milk. It is peculiar in having its optical activity and cupric oxide reducing power increased by treatment with dilute acid, and in yielding mucic acid on oxidation with nitric acid. Physically it is distinguished from other sugars by its crystalline form and sparing solubility in cold water.

Cane Sugar is well characterised by its behaviour with tests 1, 3, 4, 5, 6, and 7.

Maltose when unmixed with dextrose is distinguished from the latter by reactions 2 and 6, but if dextrose be also present only a quantitative application of tests 3, 4, 6, and 7 will suffice for the detection of maltose.

Dextrin, which often occurs together with maltose, may be detected in mixtures of the two by gradually adding a large excess of strong alcohol, when it is precipitated in flocks which often adhere to the sides of the beaker as a gummy mass. Dextrin is said to be unaffected in its optical activity by boiling with a concentrated alkaline solution of mercuric cyanide, by which treatment maltose and dextrose are oxidised and destroyed.

549. The value of the tests depending on the reduction of alkaline cupric solutions and observations of optical activity is greatly diminished when the experiments are merely of a qualitative nature, whereas an intelligent interpretation of the quantitative indications of these tests will allow of the better known sugars being not only detected but actually determined in presence of dextrin and of each other.

550. For the Determination of Sugars in admixture, the cupric oxide reducing power (K) and specific rotatory power (S) should be determined under the following circumstances:—

a. In the *original* solution of known concentration.

b. In the solution after treatment with *invertin*, as described in par. 563.

c. In the solution after heating for some hours with dilute sulphuric acid, in the manner described in par. 508.

551. The following table shows the relative cupric oxide reducing power (K) (determined gravimetrically as in par. 537) of the principal sugars, that of dextrose being taken as 100; and the specific rotatory power (S) of the solutions of the original substances, and of the inverted solutions thereof, corrected for increase in volume. The values given are in all cases calculated for the *anhydrous* substance, and the volume of the solution is assumed to remain unchanged, any dilution being duly allowed for. The characters attributed to gallisin are also given in the table:—

	Dextrose	Lævulose.	Milk-Sugar.	Maltose.	Cane-Sugar.	Dextrin.	Gallisin.
CUPRIC OXIDE REDUCING POWER (=K).							
a. Of *original* solution, .	100	100	67·8	62	0	0	45·6
b. After treatment with *invertin*, . . .	100	100	67·8	62	105·3	0	45·6
c. After heating with *acid*,	100	100	97·7	105·3	105·3	111·1	...
SPECIFIC ROTATORY POWER (for Sodium ray = S_D).							
a. For *original* solution, .	+52·7	−98·8	+55·8	+139·2	+66·5	+198	+84
b. After treatment with *invertin*, . . .	+52·7	−98·8	+55·8	+139·2	−24·3	+198 (?)	+84
c. After heating with *acid*,	+52·7	−98·8	+71·0	+ 55·0	−24·3	+ 58·5	...

It must be borne in mind that the figures representing the cupric oxide reducing powers after treatment with invertin or dilute acid are not the values of K for the original weights of substance, but for the *products of the inversion*. Thus, on heating with dilute acid, 9 parts of dextrin yield 10 of dextrose, and hence the value of K after the treatment is not 100, but $100 \times \frac{10}{9}$. Similarly, when milk sugar, maltose, or cane sugar undergoes hydrolysis, the resultant glucoses are $\frac{20}{19} = 105{\cdot}27$ per cent. of the weight of the original sugar, and hence the reducing powers and optical activity of the solutions are correspondingly increased. In the latter case, the figures in the table represent the *rotation produced by the products* of the hydrolysis, and not the actual value of S_D for those products.

552. In determining the values of K and S_D it is necessary to know the amount of sugar employed in the operation. This is

best ascertained by evaporating to dryness a known measure of the solution employed for the determinations, but in some respects there is an advantage in calculating the strength of the solution from the density. The concentration of solutions of pure cane sugar can be accurately ascertained by dividing the excess of density over that of water by 3·86, as described in par. 487, but this divisor is not strictly accurate for solutions of other carbohydrates. In practice, it is sometimes very convenient to follow the practice of Brown and Heron (*Jour. Chem. Soc.*, xxxv. 569 *et seq.*), and assume all solutions of carbohydrates to have the density of cane sugar solutions of the same strength, using appropriately modified figures to express the values of K and S_D. As the true density of a solution of dextrin containing 10 grammes of the dry solid in 100 c.c. measure is 1039·4, the value of $S_{D3\cdot86}$ will be $198 \times \frac{3\cdot86}{3\cdot94} = +194°$. Similarly, the value of $S_{D3\cdot86}$ for maltose will be $+136°\cdot4$.

553. The following is a description in outline of the mode of procedure which should be adopted in the application of the foregoing principles to the analysis of one of the most complicated saccharine mixtures likely to be met with in practice. It assumes the presence in admixture of dextrose, lævulose, sucrose, maltose, dextrin, and gallisin, together with water and mineral matter. Such a mixture would be represented by honey which had been adulterated both with cane sugar and glucose-syrup.

a. The *total solids* are estimated by evaporating a known measure of the solution to dryness in a flat dish. On deducting the *ash* left on igniting the residue the amount of the *organic solids* will be ascertained. The solids may also be deduced from the density of the solution by dividing the excess above 1000 by 3·86.

b. The *dextrin* may be precipitated by pouring the aqueous solution gradually into a large excess of rectified spirit. After standing till the precipitate is completely settled, the liquid is poured off and the dextrin estimated in the residue by direct weighing, or deduced from the solution-density or optical activity of the redissolved residue.

c. The *gallisin* may be estimated by distilling the alcoholic solution obtained in *b*, fermenting an aliquot part of the residual liquid, and treating the filtered solution left after complete fermentation by Fehling's solution.

d. The rotation due to the *sum* of the optically active bodies present is ascertained on the clarified solution at 15° C.

e. The *lævulose* is estimated from the change in the rotatory power of the solution on heating, as described in par. 671.

f. The *sucrose* is estimated from the change produced in the rotatory power of the solution by treatment with invertin (par. 563). The result is confirmed by the change in the cupric oxide reducing power of the solution caused by the action of the invertin.

g. The cupric oxide reducing power of the original solution is determined gravimetrically by Fehling's solution. From the value for K thus obtained that due to any gallisin found after fermentation is deducted, and from the remainder is subtracted the reduction due to any lævulose present. The difference is the reducing power due to the dextrose and maltose. The sum of their weights having been ascertained by deducting the lævulose, sucrose, dextrin, gallisin, and ash from the total solids, the amounts of *maltose* may be calculated by subtracting the value of K for the two bodies from the sum of the percentages of the two, and dividing the difference by 0·38.[1] The maltose thus found is subtracted from the sum when the percentage of *dextrose* will be arrived at. Further information on the estimation of dextrose and maltose in admixture is given in the section on "Commercial Glucose."

CANE SUGAR.

554. Sucrose. Saccharose. Saccharon. Cannose. Diglucosic Alcohol.

French—Sucre de Canne. *German*—Zucker.

$$C_{12}H_{22}O_{11} = \left.\begin{matrix}(C_6H\ \ O_5)\\(C_6H_{11}O_5)\end{matrix}\right\} O.$$

Cane sugar is found ready-formed in the sugar-cane and many grasses, in the sap of many forest trees, in the root of the beet and the mallow, and in several other plants. It is also found in many seeds, and notably in walnuts, almonds, hazel nuts, barley, coffee beans, &c. Most sweet fruits contain sucrose together with invert sugar, but some contain only the former.[2] The nectar of flowers

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[1] If K be the cupric oxide reducing power due to the two bodies, and P the sum of the percentages of maltose (m) and dextrose (d), then:—

$$K = d + \cdot 62m;\ P = m + d;\ P - K = \cdot 38m;\ \text{and}\ m = \frac{P - K}{\cdot 38}$$

[2] For the extraction of *sucrose* from plant-products on a small scale, the fine substance should be boiled with strong alcohol, the solution filtered hot, and allowed to cool, when the cane sugar will usually crystallise out, or can be caused to do so after concentrating the solution. If *invert sugar* be also present, Peligot and Buignet recommend the following method:—Add to the juice an equal measure of alcohol to prevent fermentation by keeping, filter, treat the filtrate with milk of lime in excess, and again filter. Boil the liquid, when calcium sucrate separates in amount corresponding to two-thirds of the

contains both, but the presence of any notable proportion of cane sugar in honey is exceptional.

555. Cane sugar forms large transparent colourless crystals, having the form of a monoclinic prism, and familiar in commerce under the names of "crystal-sugar" and "sugar-candy." The crystals have a specific gravity of about 1·6, and are unchangeable in the air.

Cane sugar exercises a powerful rotatory action on a ray of polarised light; the apparent rotatory power in 10 per cent. solutions being $+66^\circ{\cdot}5$ for the D line, and $+73^\circ{\cdot}8$ for the transition-tint. The optical properties of cane sugar are fully described in the section on the "Relations of the Sugars to Polarised Light" (see par. 455 *et seq.*).

556. At a temperature of about 160° C. (320° F.) cane sugar melts, and on cooling forms a transparent amber-coloured solid known as barley sugar. This modification gradually loses its transparency from spontaneous crystallisation, but the change may be retarded, though not altogether prevented, by the addition of a small proportion of vinegar to the melted sugar.[1]

When heated a little above 160° C. cane sugar is converted without loss of weight into a mixture of dextrose and lævulosan. $C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$.[2] At a higher temperature water is given off, the dextrose being probably converted into glucosan, $C_6H_{10}O_5$, the next stage being the formation of caramelan, $C_{12}H_{18}O_9$, which is an amorphous highly deliquescent substance, colourless when pure, having a bitter taste, and incapable of being reconverted into cane sugar by hydrolysis. Above 190°, dark coloured bodies are produced, some of which are soluble and others insoluble in water or alcohol.[3]

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whole cane sugar present. The precipitate is filtered off, washed well, diffused in water, and decomposed by carbonic acid. The solution is filtered, evaporated at a gentle heat to a syrupy consistence, decolorised by animal charcoal, and mixed with strong alcohol till it becomes cloudy, when it is set aside to crystallise. If the solution, after treatment with carbonic acid, yields a turbid filtrate, solution of basic lead acetate is added, the liquid re-filtered, and the excess of lead separated by sulphuretted hydrogen.

[1] Barley sugar appears to be a definite allotropic modification of cane sugar comparable to viscous sulphur.

[2] On dissolving the product in water and fermenting the solution with yeast the dextrose is destroyed, and by evaporating the liquid the lævulosan may be obtained as an uncrystallisable syrup, which appears to become converted into lævulose on boiling with water or dilute acids.

[3] These constitute the substance known as caramel, or "burnt-sugar," which is also obtainable from dextrose, and is employed for tinting cognac, rum, vinegar, &c., and for other colouring purposes. The dark colour of

At a still higher temperature, inflammable gases are evolved, the decomposition being attended with a highly characteristic smell.

557. Cane sugar is soluble in about one-half of its weight of cold water, forming a very sweet viscid liquid known as syrup. In boiling water it is soluble in all proportions.[1] An aqueous solution of sugar on being subjected to prolonged ebullition acquires an acid reaction, usually becoming less viscid and losing irrecoverably its power of crystallisation. The liquid then contains invert sugar. When heated with water under pressure to 160° C. sucrose is decomposed with production of formic acid, carbon dioxide, and carbon.

Cane sugar is almost insoluble in absolute alcohol, but dissolves in rectified spirit of wine with moderate facility, and readily in weaker alcoholic liquids. Weak spirit dissolves more sucrose than would be taken up by the water of it alone, but strong spirit dissolves less sugar than would be dissolved by the water of the spirit separately.

Sucrose is insoluble in ether, chloroform, carbon disulphide, petroleum spirit, or oil of turpentine, but dissolves in glycerin and all aqueous liquids.

558. The reaction of dilute acids on cane sugar results in the formation of the mixture of glucoses called invert sugar (see par. 672).

Strong sulphuric acid acts violently on cane sugar, charring it, and causing abundant evolution of gas (see par. 501).

Nitric acid acts upon cane sugar in a manner dependent on its concentration and other conditions. With one part of sugar and three of nitric acid of 1·25 to 1·30 sp. gr., the product formed at 50° C. is wholly saccharic acid, $C_6H_{10}O_8$ (par. 499), but at a boiling heat oxalic acid, $C_2H_2O_4$, is the chief product. If stronger nitric acid be employed, these bodies undergo further oxidation with formation of carbonic acid. Cold fuming nitric acid converts cane sugar into nitro-sucrose, which probably contains $C_{12}H_{18}(NO_2)_8O_{11}$. (Elliott, *Jour. Amer. Chem. Soc.* iv., 147).

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stout is due to the presence of carameloid bodies in the burnt malt from which it is brewed.

The changes undergone by cane sugar on heating furnish a good example of "cumulative resolution" thus:—

$$C_{12}H_{22}O_{11} - H_2O = C_6H_{12}O_6 + C_6H_{10}O_5. \quad \text{Lævulosan.}$$
$$C_6H_{12}O_6 + C_6H_{10}O_5 - H_2O = 2C_6H_{10}O_5. \quad \text{Glucosan.}$$
$$2C_6H_{10}O_5 - H_2O = C_{12}H_{18}O_9. \quad \text{Caramelan.}$$

[1] For information respecting the density of aqueous solutions of cane sugar, see par. 484 *et seq.*

Glacial acetic acid forms with cane sugar several acetyl derivatives, having the constitution of sucrosic acetates.

When cane sugar is rubbed in a mortar with caustic potash or soda it undergoes no visible change, a property which distinguishes it from the glucoses. Similarly, the solution of cane sugar undergoes no immediate change when mixed with alkali and raised to the boiling point. The rotatory power of the alkaline liquid is temporarily diminished, but is restored to its original amount on neutralising the solution by an acid.

When fused with caustic potash sucrose yields oxalate and acetate of potassium and other products.

According to Wanklyn, when boiled with a strongly alkaline solution of potassium permanganate cane sugar is oxidised in a very definite manner with formation of oxalic and carbonic acids, the reaction being—

$$C_{12}H_{22}O_{11} + O_{20} = 4C_2H_2O_4 + 7H_2O + 4CO_2 .$$

Cane sugar does not immediately reduce Fehling's solution at a boiling temperature, but on prolonged ebullition precipitation of cuprous oxide gradually occurs.

559. SUCRATES.

Cane sugar possesses considerable solvent powers for certain metallic oxides, with which it forms definite compounds. Thus, lime, magnesia, and litharge dissolve with some facility in syrup, but are completely reprecipitated by passing a current of carbonic acid gas through the liquid. Metallic lead is attacked by sugar solutions, slowly in the cold, but more quickly at a boiling heat, the lead passing into solution. Several sucrates of calcium are known. The solution of calcium sucrate has an alkaline and bitter taste, and forms the *liquor calcis saccharatus* of pharmacy. On mixing syrup with a concentrated solution of baryta, a crystalline precipitate is obtained, having the composition $C_{12}H_{22}BaO_{12} = BaO,C_{12}H_{22}O_{11}$, or $C_{12}H_{21}(Ba.OH)O_{11}$. This compound may be re-crystallised from boiling water, separating in brilliant scales resembling boric acid. Its sparing solubility in cold water has been utilised in the treatment of saccharine juices, pure cane sugar being readily obtainable by decomposing the barium sucrate by sulphuric acid. On adding strontium hydroxide to a boiling 15 per cent. solution of sugar, the compound $C_{12}H_{20}(Sr.OH)_2O_{11}$ begins to separate, and when $2\frac{1}{2}$ molecules of strontia have been added almost the whole of the sugar will be precipitated. The granular sucrate may be washed with hot water, and decomposed by carbonic acid. This process is now employed in recovering sugar from molasses.

Cane sugar resembles tartaric and citric acids in its power of preventing the precipitation of ferric and cupric oxides by alkalies, and the reaction has even been employed quantitatively.

560. With sodium chloride, cane sugar forms a crystallisable compound of the formula $C_{12}H_{22}O_{11}+NaCl+2H_2O$. A solution of this body has a less powerful rotatory action on polarised light than corresponds to the sugar contained in it, whilst the optical power of a solution of the compound $2C_{12}H_{22}O_{11}+3NaI+3H_2O$ is directly proportional to that of the contained sugar.

By the action of a small quantity of yeast (*Saccharomyces cerevisiæ*) sucrose in solution is transformed into invert sugar. A larger proportion of yeast converts the sugar into alcohol, carbon dioxide, and other products, the process being that known as the *alcoholic* or *vinous fermentation.* It is more fully considered in par 165 *et seq.*

561. Detection of Cane Sugar.

Cane sugar is detected more readily by its physical properties than by its chemical reactions. The following are the leading characters of service in the recognition of cane sugar :—

a. The sweet taste of the substance or solution.

b. The dextro-rotatory action of the solution on polarised light (see par. 455).

c. The form of the crystals (see par. 555).

d. The characteristic odour produced on heating the solid substance (see par. 556).

e. The production of saccharic and oxalic acids by the action of moderately concentrated nitric acid (see par. 496).

f. The formation of alcohol by the prolonged action of yeast on the warm solution (see par. 512).

g. The increase in the reducing power of the liquid on Fehling's test after inversion of the sugar by treatment with dilute acid (par. 533), and the change in the rotatory power of the solution by inversion (see par. 472).

h. The similar change in the reducing and rotating power of the solution by treatment with invertin (par. 563). This reaction is very characteristic.

For information respecting the distinctive tests for *cane sugar, milk sugar, maltose,* and *glucoses,* see par. 547.

The greater number of the foregoing properties and reactions of cane sugar receive more precise recognition in the following section on the

562. Determination of Cane Sugar.

Cane sugar may be determined by a variety of methods, which may be conveniently classified according to the principles on which they are based.

a. Determination of Sugar from the Density of the Solution.—For the employment of this method it is, of course, essential that the solvent should be water, and that sensible quantities of foreign matters should be absent; if volatile, like alcohol, they may be removed by distillation. The method is constantly applied in sugar-works, not so much for ascertaining the amount of sugar in the juice as to obtain an estimate of the foreign matters associated with it; the actual sugar being really determined by other methods, and a corresponding deduction made from the percentage of "apparent sugar" present. On page 484 *et seq.* full directions are given for deducing the proportions of cane sugar contained in aqueous saccharine solutions of various densities.

The percentage of sugar by weight having been ascertained, the number of pounds of sugar per gallon of the syrup may be found by multiplying the specific gravity by one-tenth of the percentage by weight, and dividing the product by 1000.

b. Determination of cane sugar by weighing as such.—This method is employed in Payen's and Scheibler's methods of sugar-assaying (see par. 579), and in a few other cases.

c. The Determination of cane sugar by fermentation is fully described in par. 513 *et seq.*

d. The Determination of sucrose by its reducing action after previous inversion to glucose is usually effected by heating it with hydrochloric acid (par. 477), neutralising with sodium carbonate, and estimating the resultant glucose by one of the processes described in the section on the "Reducing Action of Sugars" (par. 533). For every 100 parts of glucose thus found, 95 parts of cane sugar must be reckoned.

e. The Determination of cane sugar by observation of the rotatory action of its solution on a ray of *polarised light* has already been fully described (par. 461).

For the determination of sucrose *in presence of other kinds of sugar*, methods *a*, *c*, *d*, and *e* are incapable of direct application. If employed both before and after inversion, methods *d* and *e* afford very satisfactory means of determining cane sugar, provided that no other body is present which is apt to suffer alteration in its reducing power or optical activity by heating with dilute acid. This is not always the case, but, under such conditions, the substitution of invertin for dilute acid, as suggested by Kjeldahl, renders it possible to effect the solution of this somewhat difficult problem.

563. INVERTIN is a soluble ferment or zymase existent in yeast. It has the property of rapidly and completely effecting the transformation of cane sugar into invert sugar, but is without sensible action

on dextrose, lævulose, maltose, or milk sugar. Its behaviour towards dextrin is not so certainly negative.

For effecting the inversion of cane sugar by invertin, Kjeldahl (*Zeits. Anal. Chem.*, xxii. 588) treats 50 c.c. of the sugar solution with a little concentrated alcoholic solution of thymol, and adds a little yeast previously washed and ground up with water. The thymol completely prevents fermentation without interfering with the action of the invertin. The mixture is allowed to remain for twenty-four hours at a temperature of about 50° to 52°. It is then diluted to 100 c.c., filtered, and the cupric oxide reducing power and optical activity estimated. From the increase in the former and the change in the latter the amount of cane sugar present in the original solution can be determined.

H. T. Brown modifies the foregoing process by grinding well-washed yeast in a mortar with a little water and ether or chloroform, and adding a small quantity of the product to the sugar solution, previously saturated with ether or chloroform. The liquid is then kept at a temperature of 30° C. for half an hour, when it is filtered and examined as before. If chloroform has been employed it must be got rid of by heating the liquid before adding Fehling's solution.

Malt-extract is also without invertive action on maltose, but cannot conveniently be substituted for invertin in the above process, as the action of diastase is not sufficiently powerful.

564. **Commercial Sugar.**

The sugar of commerce is principally obtained from the sugar cane[1] (*Saccharum officinarum*), but almost equally large quantities are manufactured on the Continent from the white beet (*Beta maritima*), smaller amounts being obtained from the date palm, and sugar maple (*Acer saccharinum*), which last yields about 5 per cent. of its weight. Sugar cane contains from 12 to 20 per cent. of sugar, and the white beet from 7 to 11, and occasionally,

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[1] The process of manufacturing sugar from the cane is shortly as follows :— The cane is crushed between rollers and the expressed juice allowed to flow into a large vessel in which it is heated nearly to its boiling point. Lime is then added, when a coagulum is formed which consists chiefly of earthy phosphates, a peculiar albuminous principle, and mechanical impurities. The clear liquid is rapidly evaporated, and, when sufficiently concentrated, transferred to a shallow vessel to crystallise. The crystals are drained from the dark-coloured syrup known as molasses or treacle, and form the raw or muscovado sugar of commerce. From this intermediate product, refined sugar is obtained by redissolving the crystals in hot water, clarifying by filtration through animal charcoal, evaporating under reduced pressure, crystallising, &c. *Loaf-sugar*, *white-crystals*, and *sugar-candy* are all practically pure sucrose.

14 per cent. Sugar is also extensively manufactured in America from sorgo (*Sorghum saccharatum*), which contains from 9 to 14 per cent. of cane sugar and from 1 to 4 per cent. of glucose.

565. Commercial sucrose is met with in all conditions of purity, from the dark brown raw sugars which were formerly popular for preserving, to the almost absolutely pure forms of sugar-crystals and sugar-candy.

566. The following analyses, chiefly by Wigner and Harland, show the general character of typical kinds of commercial sugar.

Description of Sugar.	Sucrose.	Glucose.	Insoluble Matter.	Ash.	Water.	Organic Matter not Sugar.	Authority.
RAW CANE SUGARS.							
West India, . .	94·4	2·2	·1	·2	2·8	·3	W. Wallace.
Dominica, . .	88·30	3·36	...	1·22	4·95	2·17	W. & H.
Jamaica, . .	90·40	3·47	...	·36	4·22	1·55	,,
Porto Rico, . .	87·50	4·84	...	·81	4·25	2·60	,,
Trinidad, . .	88·00	5·14	...	·96	4·23	1·67	,,
Surinam, . .	86·80	4·31	...	2·28	5·27	1·24	,,
China, . . .	72·50	9·19	...	1·80	6·76	9·75	,,
Benares, . .	94·50	2·63	...	1·50	·98	·39	,,
White Java, . .	99·20	·20	...	·20	·40	trace	,,
Unclayed Manilla, .	82·00	6·79	...	2·00	5·97	3·24	,,
RAW BEET SUGARS.							
Beet (average of 7),	93·64	trace	...	1·67	2·62	2·07	J. Bell.
Beet, . . .	89·15	...	...	2·68	4·26	3·96	H. Gill.
Beet, . . .	95·70	·80	...	1·60	2·00	·40	W. Wallace.
PALM SUGARS.							
Date, . . .	95·40	1·80	1·70	·20	·80	·40	,,
East Indian, . .	86·00	2·19	...	2·88	6·04	2·89	W. & H.
SORGHUM SUGARS.							
... ...	93·05	·41	...	·68	1·72	4·14	Böckmann.
Hutchison, Kansas,	92·00	4·50	...	1·10	1·50	·90	O. Houck.
REFINED SUGARS.							
Tate's crystals, .	99·90	none	...	trace	trace	none	W. & H.
French pulverised,	99·70	trace	...	·10	·20	none	,,
Duncan's granulated, . . .	99·80	trace	...	·10	·10	none	,,
Martineau's tablets,	99·80	none	...	·10	·10	none	,,
Finzel's crystals, .	99·86	none	none	·01	·13	none	A. H. Hassall.
Beet sugar loaf, .	99·10	trace	...	·15	·25	none	W. & H.
Beet sugar crystals,	99·90	none	...	trace	trace	none	,,

567. ANALYSIS AND ASSAY OF COMMERCIAL AND RAW SUGARS.

The following are the most approved methods for the determination of the principal constituents of commercial sugars.

568. *Water* is estimated in granular cane sugars by exposing 5 grammes of the sample in a thin layer to a temperature of 60° C., weighing every hour until there is no further loss. Twelve hours are frequently required for complete dessication. Beet sugars

and good cane sugars may be dried at 100° C., two hours being sufficient. Sugars containing much glucose generally give too high a result if dried at 100° C., owing to a partial conversion of the glucose into glucosan and caramel. Large-grained refined sugars absorb moisture with great facility after drying, and should be weighed between closed watch glasses.

Some operators prefer to employ a temperature of 110° C. for estimating the water in sugar, by which means the time required is usually greatly shortened.

569. The estimation of water in treacle, beet and cane juice, &c., is tedious, owing to the low temperature which must be employed, and to the formation of a skin on the surface of the liquid. To avoid this 5 grammes (or other known weight) of the sample should be dissolved in water, and the solution made up to 100 c.c. 10 c.c. of this solution (= ·5 gramme of the original sample) are poured over about 12 or 15 grammes of previously ignited silver-sand, contained in a flat dish. The whole is dried at a temperature not exceeding 60° C. until constant, the increase in weight being due to the dry sugar in ·5 gramme of the sample. By conducting the dessication in a partial vacuum,[1] from which the moisture is removed by sulphuric acid or chloride of calcium, the operation may be finished in a few hours.

570. *The Ash* of raw sugar may contain sand and other insoluble matters of mineral origin; various inorganic salts; and the non-volatile residues of the salts of various organic acids, among which may be acetic, succinic, oxalic, malic, tartaric, citric, aconitic (in cane sugar and juice only), aspartic (peculiar to beet sugar), melassic, saccharic, &c.

The most complete analysis of sugar-ash hitherto published is one by W. Wallace (*Chem. News*, xxxvii. 76). The ash was derived from a Demerara cane sugar, the juice of which is supposed to have been treated with lime only. The raw sugar yielded 1·38 per cent. of ash, an analysis of which gave the following results, K_2O, 29·10; Na_2O, 1·94; CaO, 15·10; MgO, 3·76; Fe_2O_3, 0·56; Al_2O_3, 0·65; SiO_2, 12·38; P_2O_5, 5·59; SO_3, 23·75; CO_2, 4·06; and Cl, 4·15 per cent. Total, 101·03; less O equal to Cl, 0·93 = 100·10.

571. The complete incineration of raw sugar is very difficult to effect satisfactorily, the ash obtained being very fusible, or light and easily blown away; and, as it consists largely of potassium carbonate, it is very deliquescent, and hence difficult to weigh accurately. To avoid these inconveniences, it is usual to treat the

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[1] Laugier dries the sample at 50° C. in a current of purified hydrogen or coal-gas. For another method, see par. 717.

sugar with sulphuric acid before igniting it, by which means the ash obtained contains the bases as the comparatively little volatile, difficultly fusible, and non-deliquescent sulphates. An allowance is made for the increased weight of the ash due to the "sulphation."

The method of procedure is as follows:—If not already wet or viscous, moisten from 2 to 4 grammes of the sample all over with the least possible quantity of water, and then with a little pure and concentrated sulphuric acid. Heat the whole gently till the frothing ceases and the mass forms a dry cinder. Ignite the charred mass in a muffle at a very low red heat, and moisten the residue again with sulphuric acid when the ignition approaches completion. Continue the ignition at a low temperature till the carbon is wholly consumed, then heat to bright redness for ten minutes, and weigh when cold. From the residue thus obtained deduct one-tenth of its weight, when the remainder will be the actual ash of the sample. If *sand* or *clay* be present in sensible quantity, it must be estimated by dissolving the ash in hydrochloric acid and weighing the insoluble residue. This must be deducted from the total ash before making the correction of one-tenth.

The following figures illustrate the average composition of the ash of raw cane and beet sugars, according to Monier:—

	Average Composition of Ash.[1]	
	Cane Sugar	Beet Sugar.
Potassium (and sodium) carbonate,	16·5	82·2
Calcium carbonate,	49·0	6·7
Potassium (and sodium) sulphate,	16·0	11·1
Sodium chloride,	9·0	
Silica and alumina,	9·5	none
	100·0	100·0

572. The correction of one-tenth in the weight of the ash

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[1] The following results by Scheibler are interesting, as showing the change produced in the weight and composition of sugar-ash by treatment with sulphuric acid:—

	Beet Sugar Ash.	
	Original.	Sulphated.
Potash,	25·65	25·65
Soda,	21·62	21·62
Lime,	6·53	6·53
Silica,	0·72	0·72
Carbonic acid (CO_2),	22·87	none
Sulphuric acid (SO_3),	17·63	58·38
Chlorine,	4·48	none
	99·50	112·90
Undetermined matters, and loss,	·50	Less $\frac{1}{10}$ 11·29
	100·00	101·61

The following analyses by J. W. Macdonald (*Chem. News*, xxxvii. 127) show for the increase caused by the conversion of the carbonates and chlorides into sulphates is not strictly accurate, but is a trade practice very commonly adopted. In some cases two-tenths is deducted, or the weight of the sulphated ash is multiplied by 0·8.

According to Landolt, the ratio between the weight of sulphated ash yielded by beet sugar and the salts existing in the sugar is approximately as 1 : 2 (see par. 593).

573. As any clay or sand contained in a sample of sugar has no prejudicial effect on the refining process, it is sometimes desirable to eliminate such extraneous matters before determining the ash proper. This is done by dissolving a known weight of the sample in water, making the solution up to a known volume, filtering through a dry filter, evaporating one half of the filtrate to dryness, moistening the residue with sulphuric acid, and igniting in the usual way.

574. *Extractive Matters. Organic Matters not Sugar.*—In ordinary commercial analyses of sugars, the sum of the sucrose, glucose, ash, and water is subtracted from 100·00, and the difference called "organic or undetermined matters." Under the last denomination are included a great variety of substances, of which the chief are:—organic acids combined with bases found in the ash; certain organic

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the composition of the mixed sulphated ash obtained in the analysis of many samples of cane and beet sugar :—

	AVERAGE SULPHATED ASH.	
	Cane Sugar.	Beet Sugar.
Potash,	28·79	34·19
Soda,	0·87	11·12
Lime,	8·83	3·60
Magnesia,	2·73	0·16
Ferric oxide and alumina,	6·90	0·28
Silica,	8·29	1·78
Sulphuric acid,	43·65	48·85
	100·06	100·06

With respect to these analyses, it may be remarked that phosphoric acid was not sought for by Mr Macdonald, but representative samples with which he favoured the writer, on analysis in his laboratory showed 2·90 per cent. of P_2O_5 in the cane sugar ash, and only 0·24 per cent. in the ash of beet sugar. In the treatment of beet-juice it is usual to employ an excess of lime, which is afterwards removed by carbonic acid. Hence the phosphates of the juice would be precipitated almost entirely at an early stage of the manufacture. The proportion of phosphoric acid in the ash of a sugar might perhaps furnish an indirect indication whether the article was manufactured from cane or from beet. Raw beet sugar, however, is readily distinguished from that derived from the cane by the appearance, flavour, and the small proportion of glucose, owing to the destruction of the greater part by the employment of a large excess of lime.

bases, such as asparagine and betaïne; gummy and pectous bodies; albuminoids and soluble ferments; and insoluble organic matters, such as particles of cane, &c. Some of these impurities have no interest for the sugar-refiner, but others are very injurious. Thus the gummy matters interfere with the process of crystallisation, and the albuminoids tend to induce fermentation.

575. Although for most commercial purposes the estimation of these substances by difference is sufficient, the method is open to the objection that all the errors of the analysis are thrown on the organic matters, and that such a method makes no distinction between the harmless and injurious bodies comprised among the "organic matters not sugar." Hence even rough methods of obtaining a further knowledge of the nature and amount of these substances have an occasional value.

Walkoff obtains a comparative estimate of the organic matters in beet products by precipitating the solution of 5 grammes of the sugar in 200 c.c. of warm water by a solution of 2 grammes of pure tannin in 1 litre. The tannin solution is added from a burette, and samples of the liquid filtered from time to time, and the filtrate tested with ferrous sulphate, which gives a dark colour as soon as the tannin has been added in excess. The tannin is said to precipitate one-sixth of its weight of organic matters, but the process is chiefly valuable as a test for the comparative purity of different specimens.[1]

Another comparative method consists in precipitating the solution of sugar with a slight excess of basic acetate of lead, and weighing the precipitate produced, or the organic matters recoverable from it by decomposing it with sulphuretted hydrogen.

576. *Glucose* (invert sugar) in raw sugar may be determined by Fehling's, Knapp's, or Sachsse's method (par. 223 *et seq.*). Fehling's solution employed gravimetrically requires a somewhat longer time than some of the volumetric methods. On the other hand, the latter require that the solution shall be tolerably free from colour.

577. *Dextrose*, in a proportion greater than one-half of the total glucose, is not a normal constituent of commercial cane sugar, but is sometimes added as an adulterant (see par. 583).

578. *Sucrose* may be determined in raw sugar by the polarimetric method (par. 461 *et seq.*). In samples containing but little glucose the original reading will be sufficiently accurate for commercial purposes, but in other cases it should be supplemented by Clerget's inversion-process (par. 471).

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[1] Asparagine is not estimated in this process. The sugar solution should be perfectly neutral.

579. DIRECT ASSAY OF RAW SUGAR FOR CRYSTALLISED SUGAR.

Instead of arriving at the proportion of crystallisable sugar in a sample by estimating the cane sugar present, and deducting from that amount weights equal respectively to the glucose and to five times the ash, Payen proposed to ascertain the amount of crystallised sugar actually contained in the sample, it being assumed that the sample would contain in a crystallised state all sugar capable of being crystallised in presence of the impurities, and that this quantity could be actually obtained in a purified condition. Payen's method has been much improved by Scheibler, who operates as follows :—

Three strengths of alcohol, having specific gravities respectively of ·8488 (No. 1), ·8265 (No. 2), and ·8118 (No. 3), are first carefully prepared, and No. 1 is mixed with 5 per cent. by measure of ordinary acetic acid. All three of these liquids are completely saturated with cane sugar by keeping them in bottles filled with lumps of the best white sugar free from powder. 20 grammes of the sample are weighed out and placed in a Mohr's burette having a plug of cotton- or glass-wool at the lower end. The orifice is provided with a compression-clamp or glass-tap, which is connected by india-rubber tubing with a flask, in which a partial vacuum can be obtained by a Bunsen pump or other means. A tube filled with pumice, moistened with sulphuric acid, is attached by a cork to the upper part of the burette, and a current of warm air drawn through the apparatus for some time to remove as much of the water as possible. (This part of the process may be omitted if the original sample be tolerably dry.) The drying-tube is next removed, and the burette filled with the sugar-saturated alcohol No. 1 (specific gravity before saturation, ·8488). This is allowed to percolate slowly through the sugar till it runs into the flask colourless, or nearly so. The liquid is then just sucked out, and the residual sugar rinsed successively with No. 2, No. 3, and finally with a mixture of one-third of ether and two-thirds of absolute alcohol. The drying-tube is again attached, and warm air sucked through the apparatus till the sugar is thoroughly dried, when it is removed and weighed; or it may be washed out (without being dried) with water, the solution clarified, made up to 100 c.c., and polarised. It is very desirable to enclose the burette in a cylindrical lamp-glass or similar contrivance by which it can be surrounded with water which can be kept at 60° C. during the preliminary and final dryings in a current of air, while by filling the cylinder with water at 60° F. (=15°·5 C.), a constant temperature is readily maintained during the treatment with alcohol. The results yielded by this process are very constant and reliable if care be taken to conduct the operation at the temperature at which the alcohols were saturated, and if the sugar be well air-dried before being washed. Although yielding good results with cane sugars and superior beet sugars, the results obtained with low beets (second and third runnings) are somewhat fallacious.[1] The method assumes that all the sugar in solution in the adhering molasses will pass into the final residue of molasses.

580. The foregoing method of assaying raw sugar has been criticised by Casamajor (*Chem. News.*, xl. 74, 97, 109, 131) who, without seriously invalidating the results obtained by it, recommends the following mode of estimating crystallised sugar:—"Methyl alcohol"—by which it is presumed the author of the process means commercial wood spirit—of ·8533 specific gravity at 60° F. (=15°·5 C.), is saturated with cane sugar in the same manner as Payen's solutions. By this treatment it increases to ·8710 specific gravity. If not strictly of this density, it must be made so by appropriate addition of water or wood spirit, allowing time for the difference in the amount of sugar to become precipitated or dissolved. 19·8 grammes of the sample are then triturated in a mortar with exactly 50 c.c. of the above solution; and when all lumps and crystals are broken up, and the action is supposed complete, the liquid is passed through a dry filter, and the density carefully taken by a hydrometer or specific gravity bottle. From the specific gravity thus found (reduced if necessary to 60° F.) the corresponding percentage of alcohol by volume is ascertained (see vol. i. p. 90), and to this figure is added 22·9,[2] the sum of the two being the percentage of crystallised sugar in the sample. If the trituration of the sugar with the spirit has to be conducted at a temperature above 15°·5 C. (=60° F.), 0·1 gramme less of the sugar should be taken for every increase of 5° C. Thus, if the temperature of the laboratory be 25°·5 C., the standard weight of the sample should be 19·6 grammes instead of 19·8.

581. ADULTERATIONS OF COMMERCIAL CANE SUGAR.

The gross impurities and intentional adulterations of raw cane sugar are sometimes very considerable. Thus the raw product may contain woody fibre from the crushed cane, often much gritty sand, sporules of fungus, colonies of *Acarus sacchari* or sugar-mite, and occasionally, when in bulk, stones, old iron, and other make-weights. Starch sugar is sometimes used as an adulterant of refined sugar (see par. 583).

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[1] The process has been investigated by Wichelhaus, Eissfeld, and Stammer, who, from numerous experiments on various kinds of raw sugar, found the method gave fairly constant and accurate results, the largest variation being 1½ per cent. (*Bied. Centr.*, 1879, p. 542). Lotman has compared the process with that of calculation from coefficients. With few exceptions, Scheibler's yield is from 0·20 to 10·15 per cent. higher than by the latter method, the differences increasing as the sugars become lower in grade.

[2] This figure is the difference between 100·0 and the percentage of alcoho by volume corresponding to the specific gravity of the standard solution.

Intentional additions of sand and earthy matters are occasionally made to raw sugars, but it is very doubtful if such a fraud has ever been actually practised by a retail dealer. Formerly, when coarse brown sugar was more frequently used than is now the case, the opportunities and inducements to adulterate were much greater than at present.

The presence of *sand* and *earthy matters* is of course indicated by an excessive proportion of ash, and the incomplete solubility of the sample in water.

Fungus spores are objectionable from the extreme rapidity with which, under suitable conditions, they develop into a spreading vegetable growth, especially in presence of nitrogenous matter. Such sugar is apt to undergo fermentation and turn sour, and preserves made with it soon spoil.

582. The *Acarus sacchari*, or sugar-mite, is a small animal closely resembling the itch-insect, and, like it, capable of burrowing under the skin and producing an irritating pustular disease called the "grocer's itch," which frequently attacks those constantly employed in handling raw sugars.

The sugar acarus is possessed of great vitality, resisting the action of warm water for many hours. It is sometimes visible to the naked eye, and was found by Hassall in 69 out or 72 samples of brown sugar purchased at retail shops in London, while Dr Cameron estimated that as many a 100,000 acari were present in each pound of the sugar supplied to one of the Dublin workhouses. The acarus is wholly eliminated by the process of refining to which white and crystallised sugar are subjected. The sugar-mite is best detected by dissolving the sample of sugar in warm water, when the insect will be found adhering to the sides of the glass, or at the surface or bottom of the liquid. By observing any suspected particles with a low microscopic power, the acarus may be readily identified.[1]

583. *Starch-Glucose* has of late years been extensively employed, especially in America, as an adulterant of the lower grades of refined cane sugar. The starch sugar used is commonly a highly-converted kind, as the other varieties are too deliquescent to be

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[1] Hassall (*Food and its Adulterations*) has published drawings of the sugar acarus and sporules of fungus found in raw sugar.

suitable for the purpose. Anhydrous glucose is sometimes employed, and the adulterated sugars generally contain less moisture than the genuine sugars of the same grades, which are known as "coffee sugars," and are always sold moist. The proportion of starch sugar employed as an adulterant is usually about 20 per cent. A much smaller addition would not be remunerative.

584. If the sense of taste be first deadened by placing a pinch of pure powdered cane sugar on the tongue, and then, while the taste remains, a portion of the suspected sample be tested in the same way, the bitterish taste of starch sugar will be distinctly perceived if the specimen under examination be adulterated.[1]

If the sample suspected to contain starch sugar be placed in a beaker and stirred for a few seconds with rather less than its own weight of cold water, any hydrated glucose will be seen floating in the liquid as white specks resembling crushed wheat. Anhydrous glucose does not behave similarly, the crystals appearing as translucent as cane sugar.

585. The employment of Casamajor's alcohol method (see par. 580) does not give an accurate estimation of starch sugar in admixture with sucrose, in consequence of the difficult solubility of dextrose in wood spirit. This fact may, however, be utilised for the isolation of a portion of the glucose. For this purpose a saturated solution of dry starch sugar in "methylic alcohol" of 935 sp. gravity is prepared.[2] The sample to be tested is thoroughly dried and then stirred for two minutes with the spirit saturated with starch sugar. The cane sugar dissolves, while any admixture of dextrose remains partially insoluble. The residue is separated by decanting the liquid, and washed first with more of the spirit, and next with strong methyl alcohol.[3] It is then examined under the microscope, when any anhydrous dextro-glucose will be recognised as elongated square prisms, while the hydrated substance appears as thin plates.

586. Casamajor also recommends the following simple test for starch sugar:—Take equal quantities of the suspected sample and one known to be genuine, and add sufficient water to each to make them decidedly moist, using the same quantity of water in each case. Stir the sugar well, so as to mix it with the water and make it uniformly wet. Then heat the mixtures to a temperature between

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[1] This test may also be employed for detecting the presence of chloride of tin and other impurities in molasses or sugars, even when the proportion is very minute (Casamajor, *Chem. News*, xli. 222).

[2] 100 c.c. of such spirit will dissolve 57 grammes of starch sugar, yielding a solution of 1250 sp. gravity.

[3] Casamajor, *Chem. News*, xliii. 326.

50° and 100°, by immersing the vessels containing them in hot water. In about ten minutes the genuine sugar will appear more moist than when cold, while the adulterated sample will have sunk into a pasty, sticky mass. After cooling down, the pure sugar will look drier, while the mixture containing starch sugar will continue in the state of sticky paste.[1]

587. When examined by Fehling's solution, genuine coffee sugar will rarely cause a reduction greater than corresponds to 5 per cent. of dextrose, while a sugar adulterated with the usual dose of starch sugar will show a reduction corresponding to about 20 per cent. of dextrose. Owing to the variable composition of commercial starch sugar (see par. 692), the proportion of it present in coffee sugar cannot be deduced with accuracy from the reducing power of the sample.

588. The same difficulty arises when an attempt is made to deduce the extent of adulteration from the optical behaviour of the sample ; and, as commercial starch sugar undergoes more or less change in its rotatory power by inversion with dilute acid, Clerget's method cannot be employed for the estimation of the sucrose present.[2] Nevertheless, the polarimeter affords qualitative results of great value, and allows the fact of adulteration to be established beyond the possibility of doubt.

589. Some samples of coffee sugar adulterated with starch-glucose exert a rotation corresponding with upwards of 100 per cent. of cane sugar, owing to the high rotatory power of maltose and dextrin. Such a result is sufficient to establish the presence of starch sugar. In cases of adulteration by more highly-converted starch sugar, the direct polarimetric test will fail to indicate the existence of adulteration, but the fact will become manifest on inversion, which process will fail to produce the same change in the polarimetric reading that would ensue if only cane sugar and a small proportion of invert sugar were present.

590. Casamajor has proposed to utilise the fact that dextrose has a higher optical activity where freshly dissolved than after some time. The standard weight of sugar is dissolved in cold water, made up to 100 c.c. and the solution examined in the polarimeter with as little delay as possible. If the sugar be genuine, the rotation first observed will remain unchanged for any length of time, but if starch-glucose be present the rotatory power

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[1] This test is based on the tendency of cane sugar to form viscous uncrystallisable compounds with the glucoses and other organic bodies. As long as a mixture of cane sugar and starch glucose is kept dry it may look fair enough, but on adding water a permanent paste will be formed.

[2] Probably invertin might be employed (see par. 563).

will gradually diminish. A sample examined by Casamajor showed 100·4 when first observed. In fifteen minutes, the sugar-indication had fallen to 94·3; to 91·6 in 30 minutes; to 90·02 in 1 hour; to 89·7 in three hours; and to 89·3 in five hours, when it became stationary. After inversion, the sugar-indication was 72·7 (*Chem. News*, xlviii. 252).

591. The approximate estimation of starch sugar in admixture with cane sugar can be effected on a principle the application of which was first suggested by Chandler and Ricketts. It is based on the fact that invert sugar becomes optically inactive at 87·2° C., while the rotatory power of starch sugar is unaltered by increase of temperature. If, therefore, the sample be inverted in the usual way by heating the solution with hydrochloric acid, and the rotation be then observed at a temperature of 87·2° C., the optical activity will be solely due to the admixture of starch sugar in the sample. Unfortunately, the complex nature of starch sugar renders its rotatory power somewhat variable, but, in the kinds used for adulterating cane sugar, S_D may be safely assumed not to be in excess of +58, which figure may be used accordingly for calculating the percentage of starch sugar from the rotation observed.[1]

592. Instead of estimating the starch sugar of uncertain optical activity, the author suggests that the lævulose produced by inversion should be determined. To estimate the lævulose, a 20 per cent. solution of the sample should be inverted, heated to boiling to destroy bi-rotation, cooled, and observed in the 22-centimetre tube, at two different temperatures as far as possible removed from each other. The method of effecting this is described in par. 681. The lævulose, multiplied by 1·9, gives the cane sugar present before inversion, and the percentage thus found, added to the water of the sample and their sum subtracted from 100·00, will give the percentage of starch sugar present.

593. Sugar Confectionery.

The various forms of sweets now so extensively manufactured rarely require analytical examination except for the detection of *poisonous colouring materials*, and the use of these has greatly declined of late years.

Among the red colouring matters of sugar confectionery, red lead and vermilion have been observed, but in the great majority of cases harmless lakes are used, or else a minute quantity of aniline red.

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[1] If a 20 per cent. solution of the sample in the 22 centimetre tube show an angular rotation of 6·2 degrees, the percentage of starch sugar in the sample will be 26·7, the formula being :—

$58° = \frac{100a}{2 \times p} \times \frac{100}{20}$; or $p = 4·31\ a$; wherefore $6·2 \times 4·31 = 26·7$ per cent. of starch sugar.

Chromate of lead is not unfrequently employed as a yellow colouring agent, but gamboge is the usual pigment. Greens have been found to be produced by a mixture of chromate of lead and prussian blue, and arsenite of copper and other cuprous pigments have also been met with.

The blue mineral colouring matters are usually harmless, consisting of prussian blue or ultramarine.

The detection of the injurious colouring matters in confectionery belongs to mineral analysis, and requires no detailed description here.

Starch-glucose is very extensively employed in the manufacture of confectionery, but its use seems wholly unobjectionable unless its nature be misrepresented.

The *essences* used for flavouring confectionery are now usually of artificial origin. Their nature is described in par. 369 *et seq.* There is no evidence that the use of artificial fruit-essences, in the minute proportion necessary, is in any way injurious.

594. Molasses or Treacle.

The physical characters of this secondary product of the manufacture of cane sugar are well known.

The production of molasses is due to the long-continued heating of the saccharine juice, but the quality varies with the nature and culture of the sugar-yielding plant, and with many other circumstances. "Refiners' molasses," the syrup obtained in the refining of sugar, retains a considerable amount of sucrose, the proportion being about 35 per cent. in cane sugar molasses, and as much as 50 per cent. in that from beet-root. This is prevented from crystallising by the impurities present in the raw sugar (see par. 603). The molasses from raw cane sugar contains a considerable percentage of invert sugar, from which beet-root molasses is comparatively free, but the latter contains raffinose, $C_6H_{14}O_7$, aspartic acid, and various other bodies. The proportion of salts contained in beet-root molasses is usually 10 to 14 per cent., whereas refiners' treacle from raw cane sugar rarely contains half that proportion.[1]

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[1] Duncan and Newlands have devised an ingenious process for treating molasses, with the result of recovering from it both crystallised sugar and potash. The molasses is treated with crude sulphate of alumina, which causes the precipitation of potash-alum in the form of fine crystals, which are removed and purified by re-crystallisation. In the saccharine liquid the excess of alumina is precipitated and the free acid neutralised by

595. The following analyses show the general composition of molasses :—

	Sucrose.	Glucose.	Ash.	Water.	Organic Matters other than Sugar.	Authority.
SUGAR-CANE PRODUCTS.						
Green syrup, . .	62·7	8·0	1·0	27·7	0·6	W. Wallace.
Golden syrup, . .	39·6	33·0	2·5	22·7	2·8	,,
Treacle, . . .	32·5	37·2	3·5	23·4	3·5	,,
Molasses,	48·0	18·0	1·4	31·1	18·0	,,
,, average, .	35	10	5	20	10	J. H. Tucker.
,, refiners', .	37·5	...	...	25	...	Casamajor.
BEET-ROOT PRODUCTS.						
Molasses,	50·9	1·1	12·9	19·0	16·1	Houghton Gill.
,, average, .	50	...	10	20	20	Wigner & Harland.
,, average, .	55	trace	12	20	13	J. H. Tucker.
,, average, .	49·4	...	...	17·1	...	Payen.

596. Bodenbender found an average of 1·5 per cent. of nitrogen in beet-root molasses, of which nearly 1 per cent. existed as betaïne and proteids, and nearly the whole of the remainder as aspartic and glutaminic acids and asparagine.[1]

chalk or lime, the liquid boiled, filtered, and decolorised by animal charcoal in the usual way. The potash salts and other impurities having been thus got rid of, an abundant crop of sugar crystals is obtained on concentrating the liquid.

C. H. Gill effects the recovery of potash from molasses by adding oxalic acid, which forms a sparingly soluble acid oxalate of potassium. The oxalates remaining in solution are precipitated by lime, and the oxalic acid recovered by decomposing the calcium oxalate by sulphuric acid.

Lagrange purifies beet sugar syrup by adding baryta and phosphate of ammonium, when a dense precipitate of barium sulphate, calcium phosphate, and ammonio-magnesium phosphate is thrown down, and carries with it much of the organic and colouring matters of the syrup.

Scheibler adds excess of strontia to the molasses, when the sugar is separated as a strontium sucrate which is subsequently decomposed by carbonic acid.

[1] *Aspartic, asparaginic,* or *amido-succinic acid,* $C_2H_3(NH_2)(CO_2H)_2 = C_4H_7NO_4$, results from the action of alkalies or dilute acids on asparagine, or amido-succinamic acid, $C_4H_8N_2O_3$, a body present in the beet and many other plants. Both asparagine and aspartic acid are *lævo*-rotatory in alkaline solutions and *dextro*-rotatory in acid solutions. Aspartic acid reduces Fehling's solution. *Glutaminic,* or *amido-glutaric acid,* $(C_3H_5(NH_2)(CO_2H)_2 = C_5H_9NO_4$, is homologous with aspartic acid, and is formed by the action of dilute acids on glutamine. Free glutaminic acid is *dextro*-rotatory ($S = +10°·2$ in 2 per cent. solutions), and the solution of its hydrochloride more strongly so ($S_D = +25°·5$). A solution of the calcium salt is *lævo*-rotatory ($S_D = -4·7$ for a solution corresponding to 2 per cent. of the acid).

Vanillin has been recently recognised in beet sugar molasses, and may even be extracted from many samples of raw sugar by simple agitation with ether.

597. Rum is obtained by the fermentation of cane sugar molasses, with subsequent distillation.

Beetroot molasses is also subjected to fermentation and distillation. The residue of the distillation, termed vinasse, is remarkable for the bodies it yields on dry distillation. Besides the ordinary products obtained by the distillation of wood or coal, the ammoniacal liquor from the dry distillation of vinasse contains a notable proportion of trimethylamine $(CH_3)_3N$, together with some allied products.[1]

598. THE ANALYSIS OF MOLASSES and syrups may be effected by the methods employed for raw sugar, but certain modifications are rendered necessary by the character of the substance.

Water may be determined as described in par. 569. When no great accuracy is required, an approximation can be obtained by taking the specific gravity of the syrup, but, owing to the salts and extractive matters of molasses having different solution-densities from that of sugar, the results are seriously vitiated in many cases. The water may also be determined by Wiley's method (par. 707).

The *ash* and *organic matter not sugar* may be determined as in raw sugars (pars. 570 to 575).

Glucose may be determined in the usual way by Fehling's solution. The estimation is not seriously affected by the presence of the other organic matters, unless a very accurate result is required, in which case the solution must be clarified by means of lead, and the excess of lead removed as described in par. 532. The solution for the estimation of the glucose should be dilute.

Sucrose is best estimated by the polarimeter, as described in par. 471 *et seq.* Rather large amounts of lead solution and bone-black are liable to be required for clarification.

599. In the molasses from beet sugar (more especially) certain optically active bodies other than sugar are present. Of these, malic, metapectic, and alkaline solutions of aspartic acid are lævo-rotatory, besides invert sugar and beet gum. Dextran, asparagine, glutaminic acid, and acid solutions of aspartic acid exercise a right-handed rotation. These interfering substances, of which the dextran and beet-gum are the most optically active, tend in great measure to

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[1] *Jour. Chem. Soc.*, xxxvi. 912, and xxxviii. 159. See also an interesting lecture by H. E. Roscoe, on "A New Chemical Industry," *Chem. News*, vol. xxxix. p. 107.

neutralise the effect of each other. The optical effect of asparagine is said to be completely neutralised by adding 10 per cent. of acetic acid to the solution filtered from the lead precipitate.

600. If one-half the standard weight of syrup be weighed out, treated with 1 c.c. of lead solution, and the mixture made up to 50 c.c. by absolute alcohol and filtered, all the asparagine, aspartic acid, malic acid, beet-gum, and dextran remain in the precipitate, while the presence of the alcohol in the filtrate is said to neutralise the rotation due to the invert sugar. The method affords a simple means of obtaining a comparatively pure solution which can be at once polarised, or the alcohol may be distilled off and the residue further treated.

The sucrose may also be determined by Fehling's solution, after previous inversion and allowing for the glucose determined without inversion.

601. Sugar-Cane and Beet Juices.

The juice obtained by crushing and pressing the sugar-cane[1] has usually a density of 1070 to 1090, but has been met with as low as 1046 and as high as 1110. It is an opaque, frothy,

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[1] The following analyses show the general composition of the sugar-cane :—

Locality and Kind of Cane.	Water.	Sugar.	Woody fibre.	Salts.	Authority.
Martinique,	72·1	18·0	9·9		Peligot.
Guadaloupe,	72·0	17·8	9·8	0·4	Dupuy.
Havana,	77·0	12·0	11·0	...	Casaseca.
Cuba,	65·9	17·7	16·4	...	Casaseca.
Mauritius,	69·0	20·0	10·0	1·0	Icery.
Ribbon cane,	76·73	13·39	9·07	·39	Avequin.
Tahiti,	76·08	14·28	8·87	·35	Avequin.

The following is a more detailed analysis by Payen of Otaheite cane a maturity :—

Water,	71·04	per cent.
Sugar,	18·00	,,
Cellulose, ligneous matter, pectin, and pectic acid,	9·56	,,
Albuminous matters,	0·55	,,
Cerosin; red, green, and yellow colouring matters; fatty matter; resins; essential oil; aromatic matter; and a deliquescent substance,	0·37	,,
Insoluble salts, 0·12; soluble, 0·16, consisting of phosphates, sulphates, chlorides, oxalates, acetates, malates, &c.,	0·28	,,
	100·00	

According to Casaseca, the lower portions of the sugar-cane are the richest in sugar, the centre being of about the average composition. This is shown yellowish green liquid. On filtration it yields a pale yellow fluid, which is nearly pure syrup, the greenish scum containing chlorophyll, a peculiar wax called cerosin, albuminous matters, fibre, and a considerable proportion of mineral matter. The pure or nearly colourless juice from which the green matter has been separated contains in 100 parts:—water, 81·00; sugar 18·20; organic matters precipitated by lead salts, 0·45; and mineral matters, 0·35.

602. The specific gravity of the juice from the white beet[1] is

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by the following analysis by Gill of carefully sampled good average cane from the Aska district, Madras :—

	A. Two feet top.	B. Two feet middle.	C. Two feet root.
Megass proper, .	7·63 per cent.	8·47 per cent.	8·30 per cent.
Juice, . . .	92·37 ,,	91·58 ,,	91·70 ,,
Containing, Cane Sugar	10·63%	13·31%	13·37%
,, Glucose .	2·64%	1·51%	1·54%

The expressed juice had the following composition :—

	A.	B.	C.
Cane Sugar, . .	11·51	14·55	14·58
Glucose, . . .	2·86	1·65	1·68
Ash, . . .	·33	·28	·25
Unknown, . .	·50	·92	·49
Apparent solids, .	15·20	17·40	17·00
Water, . . .	84·80	82·60	83·00
	100·00	100·00	100·00

The megass referred to above contains little but woody fibre, as the sugar extracted in the Aska district by the diffusion process. Ordinary megass or mill-trash after passing the rollers retains 8 or 10 per cent. of sugar and 50 per cent. of water.

The *ash* of the sugar-cane contains about 50 of silica, 5 to 8 of phosphoric acid, and very variable proportions of potash. Soda appears to be a constant constituent.

[1] The following is an analysis by Payen of the white or sugar beet :—

Water, ...	82·7 per cent.
Sugar, ...	11·3 ,,
Cellulose, ...	0·8 ,,
Albuminous matters, ...	1·5 ,,
Fatty matter, ...	0·1 ,,
Pectin matters, asparagine, aspartic acid, betaïn $(C_{15}H_{33}N_3O_6)$, &c. ; oxalates, nitrates, phosphates, &c., ...	3·7 ,,
	100·0

usually between 1060 and 1070, occasionally reaching 1078. Beet juice contains a large amount of foreign matters in proportion to the sugar, a fact that renders the manufacture of sugar from beetroot much more troublesome than from cane. The average percentage composition of expressed beet juice is approximately:—water, 84·68; sugar, 11·25; other organic matters, 1·47; and mineral matters, 0·67.

THE ANALYSIS of cane and beet juices may be effected by the method described under "Molasses" and "Raw sugar."

603. Valuation of Cane and Beet Products.

Two samples of sugar containing the same percentage of sucrose often differ considerably in their yield of crystallisable sugar when refined. This is attributable to the varying nature and quantity of the salts and other impurities, which either tend to destroy the sucrose by inversion or prevent its crystallisation. These considerations resulted in the adoption of the assumption that each unit of ash prevents five units of cane sugar from crystallising, and that each unit of glucose prevents the crystallisation of an equal weight (or according to some practices twice its weight) of cane sugar. Hence a deduction equal to (twice) the percentage of glucose found, *plus* five times the weight of the ash, must be made from the content of cane sugar found by analysis, in order to ascertain the percentage of nett obtainable or crystallisable sugar in the sample.[1] This percentage of crystallisable sugar is called the "refining value" of the sample. The results of the above calculation are not always in strict accordance with the truth, though for beet sugar the variations are not great. Schultz considers that the out-turn of refined beet sugar is equal to the total sugar *minus* twice the amount of total soluble impurities.

604. A rapid approximate valuation of sugar may be obtained by making a perfectly saturated solution of the sample in water at 17·5° C., and ascertaining the density of the liquid. In the case of pure cane sugar this will not exceed 1330·0; but the specific

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[1] A commission appointed by the French Government recommended the following plan of valuing raw sugars, which is now the officially recognised method in France, though it has not met with general acceptance in other countries, as its indications are liable to be erroneous in the case of cane sugar. From the percentage of sucrose shown by the polarimeter is subtracted the sum of:—

a. Four times the weight of the ash. (By "ash" is meant sulphated ash multiplied by 0·8). *b. Twice* the glucose when the latter reaches 1 per cent.; or a weight *equal* to the glucose when the latter is between ½ and 1 per cent. When the glucose is below 0·5 per cent. the correction *b* is neglected. *c.* 1½ per cent. for waste in refining.

gravity increases with the proportion of foreign substances. The following table is given by E. Anthon (*Jahresb.*, 1868, p. 957):—

Specific gravity of Saturated Solution.	Percentage composition of solution saturated at 17·5° C.		
	Sugar.	Other substances.	Water.
1330·0	66·66	0·00	33·34
1332·2	64·85	2·66	32·49
1338·4	63·70	5·29	31·01
1344·6	62·65	7·76	29·68
1350·9	61·42	10·13	28·45
1357·2	60·28	12·48	27·24
1363·6	59·14	14·67	26·19
1370·0	58·00	16·82	25·18
1376·4	56·85	18·87	24·28
1382·9	55·70	20·77	23·53
1389·4	54·56	22·59	22·85
1395·9	53·42	24·36	22·22
1402·5	52·28	25·98	21·74
1409·2	51·14	27·56	21·30
1415·9	50·00	29·00	21·00

605. A very convenient and instructive method of assaying a *juice*, *syrup*, or *molasses* is to ascertain the ratio which exists between the percentage of sugar as determined by the polariscope and as deduced from the density of the liquid. The difference between the two results is the percentage of "solids not sugar," and though the non-identity of the solution-density of these matters with that of sugar prevents the method from giving really accurate results, it affords a very simple and practical means of judging of the relative purity of saccharine liquids, and calculating the amount of crystallisable sugar obtainable therefrom. The percentage of "apparent sugar," or total solids in the liquid, can be deduced from the table of densities in par. 490, and this figure multiplied by the density of the solution gives the number of grammes of total solids per 100 c.c. This result may also be obtained from the formulæ on page 211, but for very strong saccharine liquids, such as molasses, the use of the table is preferable. From the contents of the liquid in total solids thus found, there is subtracted the number of grammes of sugar per 100 c.c. found by the polarimeter, when the difference is the "solids not sugar" per 100 c.c. The percentage of real sugar contained in 100 parts of total solids or "apparent sugar," is called the "apparent-purity-coefficient" of the juice.

In the case of cane-juice products, the "solids not sugar" are found in practice to prevent the crystallisation of an equal weight of sugar, but 1 per cent. of the "solids not sugar," from beet-root will prevent the crystallisation of 1·2 per cent. of sugar. Hence a sugar-cane product having an apparent-purity-coefficient of less than 50 cannot be made to yield any crystallisable sugar, and the same is true of a beet-root product having a coefficient somewhat greater than this.[1] By removing the salts (see footnote, page 256), even molasses can be made to yield crystallised sugar.

606. MALT-SUGAR.

Maltose, Malton, $C_{12}H_{22}O_{11}$.

The sources and leading properties of this sugar are given on page 192. It has been comparatively recently isolated in a state of purity, the existing knowledge respecting it being largely due to the researches of C. O'Sullivan (*Jour. Chem. Soc.*, xxix. 479, xxx. 125). By this and other chemists it has been definitely proved that the action of diastase on starchy matters (*e.g.*, malt, maize, rice) gives rise to a production of maltose and dextrin. Hence malt-worts do not contain dextrose or other variety of glucose, as commonly supposed, but a mixture of dextrin, $nC_6H_{10}O_5$, and maltose, $C_{12}H_{22}O_{11}$, both of which may be converted into dextrose by heating with dilute acid.

607. Maltose usually occurs in fine crystalline needles, which contain $C_{12}H_{22}O_{11},H_2O$, and become anhydrous at 100° C., yielding an extremely hygroscopic residue. In alcohol, maltose dissolves with less facility than sucrose.

608. The specific rotatory power of maltose has been determined by various observers with the results shown on the following page. The values printed in prominent type are those obtained by direct observation; the others by the calculation that $S_j : S_D = 1·00 : 1·11$. There is no doubt that some of the lower determinations recorded in this table apply to crystallised maltose, and for this and other reasons the higher numbers are more probably correct. Hence in this work the apparent specific rotatory power of maltose will be represented by the value $S_D = 139·2$, and $S_j = 154·5$.[2]

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[1] Thus, if a beet-juice have a coefficient of 79, the residue on evaporation will contain 79 per cent. of sugar and 21 of impurities. $21 \times 1·2 = 25·2$, which deducted from 79 leaves 53·8 as the percentage of the total solids obtainable in the form of crystallisable sugar.

[2] In some cases it is convenient to calculate the rotatory power of maltose on the assumption that a solution containing 10 grammes for 100 c.c. has a density of 1038·6. In this case $S_{D.3·86} = +136·4$, and $S_{j3·86} + 151°·3$, or according to H. T. Brown + 150°.

Apparent Specific Rotatory Power of Maltose in Aqueous Solution, as determined by different observers.

Value for Anhydrous Sugar of		Concentration of Solution employed.	Observers.
S_D.	S_j.		
134·3	149·0	...	Musculus & von Mering.
134·7	149·5	...	E. Schulze.
133·7	148·4	...	E. Külz.
135·7	150·25	6 to 10	H. Yoshida.
135·2	150·0	various	E. Sandwik.
139·2	154·5	10	C. O'Sullivan.
138·0	153·1	5	Brown & Heron.
139·0	154·3	5	A. Herzfeld.
139·3	154·6	...	Soxhlet.
139·3	154·6	20	E. Meissl.
138·9	154·2	11	I. Steiner.

The rotatory power of freshly-made solutions of maltose is less than that of solutions which have been kept some time or heated. A cold solution of maltose does not acquire its full optical activity for several hours, a fact which must be borne in mind in practice. A similar "bi-rotation," or change of optical activity, is observed with solutions of milk sugar and dextrose, but in their cases the rotatory becomes less by keeping, instead of increasing as with maltose.

The rotatory power of maltose varies to but a slight extent with the temperature and concentration of the solution.[1] The concentration, or grammes of anhydrous maltose per 100 c.c. of solution, can be found as described in par. 488.

609. When heated with dilute acid, maltose gradually undergoes hydrolysis by conversion into dextrose, the solution increasing in reducing power and diminishing in optical activity. Boiling for five minutes with dilute sulphuric acid causes a notable change, but complete inversion is effected less readily than in the case of sucrose, and requires a treatment for three or four hours at the ordinary pressure (see also par. 507). Malt-extract and invertin do not invert maltose.

610. Maltose is probably incapable of direct fermentation, but by the continued action of yeast its conversion to dextrose and fermentation go on simultaneously, and it yields alcohol to the amount of 51 to 51½ per cent. of the original weight. If a

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[1] Meissl gives the formula $S_D = 140·375 - 0·01837c - 0·095t$, in which c is the number of grammes of maltose per 100 c.c. and t the temperature, centigrade. These corrections are insignificant.

mixture of maltose and dextrose be fermented with yeast, the whole of the glucose disappears before the former sugar is touched.

611. Maltose forms compounds with the alkalies and alkaline earths, and also gives an octo-acetyl-derivative, $C_{12}H_{14}O_{11}(C_2H_3O)_8$, which crystallises in thin prisms and possesses a rotatory power of $+81°·2$ for the sodium ray, when dissolved in benzene.

Maltose does not appear to unite with borax, or with sodium chloride or bromide.

Chlorine or bromine in presence of water acts less readily on maltose than on dextrose or sucrose, but eventually converts it into gluconic and glycollic acids.

612. Maltose resembles the glucoses in its power of reducing hot Fehling's solution without previous inversion, but the amount of cuprous oxide precipitated is only 62 per cent. of that reduced by an equal weight of dextrose.[1] Soxhlet states that the cupric oxide reducing power (K) is 61 when the maltose is contained in a 1 per cent. solution, and the Fehling reagent is undiluted and employed in the exact proportion necessary; 64·1 when the copper solution is previously diluted with four volumes of water; and 65·3 when twice as much of this diluted Fehling's solution is used as is required for the reaction (*Jour. Pr. Chem.*, [2] xxi. 227 *et seq.*).

613. When a solution of maltose is treated with a measure of Fehling's solution sufficient for its oxidation, the mixture heated, and the cuprous oxide filtered off in the usual way, a solution is obtained which, if acidulated with hydrochloric acid and heated, acquires the property of reducing an additional quantity of Fehling's solution. This second reduction is somewhat more than half the first, so that the two together approach to the reducing power of dextrose. A similar behaviour is exercised by milk sugar (Herzfeld, *Ann. der Chem.*, ccxx. 206).

614. According to I. Steiner, the reducing action of maltose on Pavy's ammoniacal cupric solution is the same as upon the ordinary Fehling's reaction. Thus, 20 c.c. of Fehling's solution requires the same measure of maltose solution for its reduction, whether it be used direct or previously mixed with 40 c.c. of strong ammonia, and titrated as described in par. 539 (Yoshida,

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[1] 60·8 is the reducing power of maltose according to Brown and Heron, and assuming 1038·6 to be the density of a solution of maltose containing 10 grammes per 100 c.c. Correcting this for the true density found by them (1039·3) the value of K becomes 61·9 (*Jour. Chem. Soc.*, xxxv. 618), C. O'Sullivan originally gave 65 as the number representing the cupric oxide reducing power of maltose (*Jour. Chem. Soc.*, xxx. 126), but in a recent letter to the writer he states the value at 62·5, and takes 1039·5 as the density of a 10 per cent. solution of maltose.

Chem. News, xliii. 29). On the other hand, the addition of more caustic soda in presence of ammonia increases the oxidising power of the cupric solution to a notable extent (*Chem. News*, xlii. 45).

The action of maltose on the mercurial solutions of Sachsse and Knapp is described in par. 543.

615. Impure maltose is now manufactured on a large scale by the action of malt-infusion on starch. The relative proportions of maltose and dextrin, produced by the action of malt-extract or dilute acids on starch, vary with the temperature employed for hydrolysis; but the normal reaction may be represented in its simplest form as follows:—

$$\underset{\text{Starch.}}{C_{18}H_{30}O_{15}} + H_2O = \underset{\text{Dextrin.}}{C_6H_{10}O_5} + \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}}.$$

This equation corresponds to a formation of 33·33 of dextrin and 70·37 of maltose from 100·00 of starch, and represents the approximate proportions of the leading constituents of a well-made beer-wort, and also of the commercial product known as "dextrin-maltose."

616. *The detection of maltose* and its distinction from the other principal sugars are considered in par. 547 *et seq.* Its determination is based on the same principles as those applied to other sugars,—namely, the density of the solution, the cupric oxide reducing power, and the action of the liquid on polarised light. The estimation of maltose in starch-sugar is described in par. 696; its determination in beer-wort in par. 635. The information in these two sections will indicate the methods employed for the estimation of maltose in all cases of practical interest.

617. **Malt.** *French*, Drèche. *German*, Malz.

Malt is prepared by steeping barley or other grain in water, and allowing it to germinate, the sprouted grain being subsequently dried in a kiln.

	Barley.	Malt.		
	Air-dried.	Air-dried.	Pale Kiln-dried.	High Kiln-dried.
Starch,	67·0	58·1	58·6	47·6
Dextrin,	5·6	8·0	6·6	10·2
Sugar,	0·0	0·5	0·7	0·9
Cellulose, &c.,	9·6	14·4	10·8	11·5
Albuminoids, &c.,	12·1	13·6	10·4	10·5
Fat,	2·6	2·2	2·4	2·6
Ash,	3·1	3·2	2·7	2·7
Torrefaction products,	0·0	0·0	7·8	14·0
	100·0	100·0	100·0	100·0

The foregoing analyses by Oudemanns illustrate the composition of unmalted barley as compared with malt dried in different ways. Apparently the constituents are calculated on the moisture-free samples.

The figures in Oudemanns' analyses, though of value for purposes of comparison, are not in accordance with the most recent knowledge of the composition of malt. Thus, O'Sullivan states that malt contains no ready-formed dextrin, but that it does contain from 16 to 20 per cent. of fermentable sugar, of which about one-half is probably maltose and due to the transformation of starch in the malting process, while the remainder exists ready-formed in the barley, and is not identical with the sugar produced in the malting.

618. The following are analyses of two samples of pale malt by O'Sullivan. Every constituent was determined directly:—

		No. 1.		No. 2.
Starch,		44·15		45·13
Other carbohydrates (of which 60 to 70 % consist of fermentable sugar), inulin (?), and a small quantity of other bodies soluble in cold water,		21·23		19·39
Cellular matter,		11·57		10·09
Fat,		1·65		1·96
Albuminoids—				
a. Soluble in alcohol (sp. gr. 820) and in cold water,	·63		·46	
b. Soluble in cold water and at 68° C.,	3·23		3·12	
c. Insoluble in cold water, but soluble at 68° to 70° C.,	2·37		1·36	
d. Insoluble at 68° to 70° C., but soluble in cold water (=albumin proper),	·48		0·37	
e. Insoluble in cold water, and at 70° C.,	6·38		8·49	
		13·09		13·80
Ash,		2·60		1·92
Water,		5·83		7·47
		100·12		99·76

619. Well-malted barley is always yellow, occasionally intermixed with a speck of brown; while a yellowish grey tint is always objectionable. On breaking the malt, the interior should be of a pure white colour, unless the drying has been intentionally carried so far as partially to caramelise the sugar.

The taste of malt is an important criterion of its quality. It should always have an agreeable, sweet taste, and the rapid perception of sweetness proves the presence of a sufficient proportion of diastase.

Malt ought to float on cold water. It should not be very hard, being easily bruised between the fingers, but should be crisp, not soft. These characters indicate whether a sample is "steely," or incompletely malted.

Good malt is plump, long and narrow corns yielding little extract. The *acrospire* should be from two-thirds to three-fourths of the length of the corn, but in no case should it protrude, otherwise too much albuminous matter will be extracted in mashing.[1]

False ferments may be recognised by washing about five grammes of the sample in a little water and examining these washings, after about a quarter of an hour's standing, under the microscope. Lactic ferments are certain to be present, but they should not be numerous or dart about in a very active manner, or the converting power of the diastose will be deficient, and the fermentative activity and purity of the yeast will suffer in consequence.

620. Chemical Examination of Malt.

The brewing value of a sample of malt is chiefly dependent on three factors, namely, the proportion of soluble or extractive matter it will yield to water; the character of this extractive matter; and the diastasic activity.

The proportion and composition of the extractive matter are influenced by a variety of conditions, including the temperature of water used for mashing; the character of the water; the proportion employed; the composition of the original malt; the temperature at which it was dried; &c.[2]

621. *Extractive Matter* in malt is best determined by a miniature mashing process, in which the same conditions are rigidly adhered to for all samples, so as to make the test strictly comparative, and to afford a criterion of the probable behaviour of the malt on a large scale. The extraction is best conducted in the following

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[1] The microscopic characters of malt at various stages of the manufacture have been described by G. L. Barb (*Pharm. Jour.*, [3] xv. 33).

[2] The following analyses by C. Graham show the influence of high kiln-heats on the character of the infusion-products subsequently yielded by the malt.

	80° C.	100° C.	120° C.
Maltose,	57·01	52·44	51·32
Dextrin,	14·92	18·49	19·35
Lactic Acid,	0·56	0·49	0·31
Soluble Albuminoids,	2·09	1·60	1·50
Colouring matters, ash, &c.,	1·49	1·38	1·32
Total dry solids,	76·07	74·40	73·80

manner:—The malt is crushed in a small coffee-mill, the fluted rollers of which are so fixed as to produce a grist which will pass through a sieve having apertures $\frac{1}{16}$th inch in diameter. 50 grammes of the product are then weighed out as rapidly as possible (to avoid accession of moisture), and treated in a weighed beaker with 250 c.c. of warm distilled water of such a temperature that the initial heat of the mixture may be from 50° to 52° C. The beaker containing the mash is placed in a water bath, and the contents maintained at the same temperature for a quarter of an hour. The heat is then gradually raised till the immersed thermometer registers 59° or 60° C., and the temperature is then kept constant till a drop taken from the liquid ceases to give a blue colour with iodine solution, and nearly ceases to give a brown. This shows that all the starch and nearly all the erythrodextrin have suffered hydrolysis,—a point which will be reached in about twenty minutes. The heat is then increased to about 70° C., in order to complete the saccharification, when the water in the bath is boiled for five minutes. This step, which completes the process of mashing, should be arrived at in about 100 minutes from the commencement of the operation. The beaker is then cooled, and the contents filtered. The insoluble matter is washed with cold water and the filtrate is made up exactly to 400 c.c. The density of the clear wort is next taken at 60° F. (= 15·5° C.) in the usual way, by a specific gravity bottle. The excess of density over that of water (taken as 1000) multiplied by 2·078, will give the percentage of dry extract yielded by the malt.[1]

Instead of ascertaining the gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish, so that the residue may form a thin film. The extract is dried at 105° C. till constant in weight. Operating in this way, C. Graham finds the dry solids of malt extract to have a solution-density of 1037·5, and not 1038·5 as generally stated.

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[1] This method is based on the fact that each gramme of malt-extract per 100 c.c. of infusion raises the density of the liquid by 3·85 degrees (water being 1000). The figure 2·078 is the fraction $\frac{8}{3·85}$; and hence the percentage of extractive matter in a sample yielding a wort of 1033 density under the conditions prescribed in the text will be:—$(1033 - 1000) \times 2·078 = 68·57$ per cent.

According to C. Graham the factor 2·078 is too low and should be 2·133, while O'Sullivan considers the factor 2·026 would be more accurate.

For most purposes, it is sufficiently accurate to make up the unfiltered wort to 415 c.c., filter a portion through a dry filter and take the density. The draff is here assumed to measure 15 c.c., and the washing is dispensed with.

The solids of malt-extract average 70 per cent. of the weight of malt from which they are derived.

The colour and flavour of the infusion obtained by the mashing should be carefully noted. If desired, the proportions of the leading constituents may be ascertained as described in par. 633 *et seq.*

622. The *nitrogenous matters* of malt are of considerable importance. Malt contains both soluble and insoluble nitrogenous compounds, the latter of which remain with the draff or grains, while the former pass into the wort, and remain to some extent in the finished beer. The presence of too large a proportion of albuminoids renders beer liable to change and "turn," while too little is disadvantageous in other respects. The coagulation of the albumin materially assists the clarification of the hot wort. The fulness on the palate, the viscosity, and the nourishing properties of beer are characters largely dependent on the albuminoids.

The total nitrogen of malt is best ascertained by igniting it with soda-lime in the usual way. The nitrogen found may be calculated to albuminoids by multiplying it by the factor 6·33. The insoluble nitrogen is ascertained from a combustion of the draff with soda-lime, and the difference between this result and the total gives the soluble nitrogen.

The proportion of total nitrogen in malting barley should be equivalent to fully 10 per cent. of albuminoids, but in practice it varies from the equivalent of 6 or 7 up to 17 per cent. of proteids.

C. Lintner (*Dingl. Polyt. Jour.*, ccli. 225) considers that the *total* nitrogen of malt bears no relation to the diastasic value, but that the proportion of *soluble* albumin is of importance in this connection. By assuming the soluble albumin to belong to the diastase, and multiplying this by 6·33, the "diastase" or soluble albuminoids in malt are found to average about 2 per cent. on the dry substance.

623. C. Graham utilises Wanklyn's "albuminoid-ammonia" process of water-analysis for the assay of malt for soluble proteids, and places much confidence in its indications. In a communication to the author he gives the following details of manipulation. The wort from 10 grammes of malt is diluted to 1000 c.c., and of this solution 10 c.c. measure (=0·1 gramme of malt) is added to 700 c.c. of water and the liquid boiled with the addition of some previously ignited sodium carbonate. When the distillate is nearly free from ammonia, 100 c.c. of Wanklyn's alkaline permanganate solution is added and the distillation continued. The ammonia in the distillate is estimated by Nessler's solution, and the amount found multiplied by 5200 gives the percentage of *soluble proteids* yielded by the malt.

624. *Draff* or *insoluble matter* may be determined by washing, drying, and weighing the residue left undissolved in the mashing operation (par. 621). It may also be ascertained by subtracting the sum of the solid extract and moisture from 100. It is found, however, in practice that the solid extract, moisture, and draff by direct weighing always amount to more than 100. This is due to the fact that the starch takes up the elements of water during the mashing, and yields more than its own weight of maltose. Hence care should be taken to describe the soluble matter as "extractive matter yielded by mashing the malt," and not as "extractive matter contained in the malt."

The "grains," "draff," or exhausted malt will have a composition varying within certain limits according to the skill with which the process of mashing or infusion was conducted. The draff from highly-dried malt contains a smaller proportion of starch than that from pale malt. Grains usually contain from 4 to 6 per cent. of albuminoids, from 5 to 10 of starch, &c., 6 to 10 of cellulose and lignin, and nearly 80 of water.

625. *Moisture* may be determined by drying a known weight of the sample in the water-oven till no further loss of weight ensues. Malt is very hygroscopic, and hence care must be taken that the moisture is determined in such a manner as fairly to represent the bulk. Freshly made English malt contains from 2½ to 3½ per cent. of moisture, which increases gradually with keeping to about 5 or 6 per cent. German and Austrian malts are not so highly dried as English, and thus often contain 5 or 6 per cent. of moisture even when freshly made, while in Bavarian malt the moisture sometimes rises as high as 10 per cent.

626. *Ash* may be determined by carefully incinerating 5 or 10 grammes of the malt sample in a muffle, at as low a temperature as possible. In some cases it is of interest to ascertain separately the mineral constituents of the draff and the infusion.

627. *The acidity* of malt is an important character in judging of its soundness. The normal proportion of free acid (calculated as lactic acid) is not more than 0·2, or at the most 0·3 per cent.; 0·4 per cent. is unusually high, and denotes unsoundness. Such malt should never be used for brewing beers intended for exportation or long keeping. The acidity of malt is readily ascertained by treating 50 grammes of crushed malt with 100 c.c. of cold water and stirring the mixture occasionally during half an hour. The liquid is then passed through a dry filter, and, when the greater part has run through, 50 c.c. are titrated with litmus or phenolphthaleïn, and decinormal soda or standard Excise ammonia. Each 1 c.c. of decinormal soda used for the neutralisation corre-

sponds to ·0090 grammes of lactic acid, $C_3H_6O_3$, in the solution operated on.

628. The *diastasic* or *hydrolytic power* of malt can be measured in the following manner:—50 grammes weight of the crushed sample is treated with 500 c.c. of cold water, the mixture being occasionally stirred during one hour. The solution is then heated to 60° C., kept at that temperature for half an hour, and the solution filtered through a dry filter. Two quantities of bread of 50 grammes each, taken from the same loaf, are treated with 300 c.c. of water at 40° C. To one of these quantities 200 c.c. of the malt infusion (=20 grammes of malt) is added, and to the other 200 c.c. of water. Both mixtures are then rendered faintly alkaline by a few drops of bicarbonate of sodium, and kept at 40° C. for three hours, when the liquids are filtered. 50 c.c. of each of the filtrates is then evaporated to dryness at a steam heat and the residue weighed. The difference between the weights of the two extracts shows the amount of matter rendered soluble by the diastase in 2 grammes of malt. The result so obtained requires a correction for the weight of solid matter in the malt extract added. This may be avoided by adding to the filtrate from the blank experiment, during evaporation, 20 c.c. of the infusion of malt, this being the quantity contained in the 50 c.c. evaporated in the other experiment.

The methods described in par. 644 for estimating the diastasic power of malt extract may also be employed for the assay of malt.

629. MALT-WORTS.

By the Inland Revenue Act of 1880, a bushel of average malt is assumed to weigh 42 pounds, and two such bushels (=84 pounds) are considered to be capable of yielding one barrel (=36 gallons) of wort of the standard density of 1057. Hence, a quarter (=8 bushels) of malt is supposed capable of yielding 4 barrels (=144 gallons). Wort of this density contains 14 per cent. by weight, or 148 pounds per 100 gallons, of solid extract. Hence the solid extract in 36 gallons of the wort will be 53·28 lbs., which is equal to a yield of 63·43 per cent. on the malt. It is further assumed that 336 lbs. of any description of grain, or 224 lbs. of sugar, are equivalent to 8 bushels (=1 quarter) of malt of an average weight of 336 lbs., and hence are also capable of producing 4 barrels of wort of 1057 specific gravity.

630. In the laboratory, the specific gravity of beer-worts is most accurately ascertained by the specific gravity bottle (par. 6), and from the result the proportion of *total solid matter* in the wort may be deduced by deducting 1000 from the figure representing the density and dividing the difference by 3·85. The dividend is the numbers of grammes of solid extract contained in

100 c.c. of the wort.[1] For the purposes of the brewer the specific gravity of the wort may be ascertained by the hydrometer, various modifications of which have been devised for this purpose.[2]

631. Bates' Brewers' Saccharometer is an instrument the indications of which are expressed in "pounds per barrel," and these may be translated into absolute specific gravities by dividing the number of "saccharometer-pounds" by 0·36 (or multiplying by 2·778) and adding 1000. A barrel ($=36$ gallons) of water weighing 360 pounds, a beer-wort a barrel of which weighs 380 pounds ($=360+20$) is said to have a "saccharometer-gravity of 20 lbs. per barrel." The real specific gravity of such wort would be 1055·5;—for $360 : 380 = 1000 : 1055{\cdot}5$; and it would contain 14·4 grammes of solid extract per 100 c.c., or 51·9 lbs. per barrel of 36 gallons. Similarly, a wort of 1057 specific gravity, which is the standard strength of beer-wort on which the duty of 6s. 3d. per barrel is levied, has a saccharometer-gravity of 20·52 lbs. per barrel; for $1057-1000=57$; and $57 \times 0{\cdot}36 = 20{\cdot}52$.

632. Corrections of densities of beer-worts for temperature can be made as described in par. 491.

The method of ascertaining the original gravity of beer-worts which have undergone fermentation is described in page 98 *et seq.*

633. The solid matter of ordinary malt infusions contains about 63 per cent. of maltose, but, when obtained in the manner directed in par. 621, the proportion is not unfrequently somewhat higher. The remainder of the solid matter consists of dextrin, albuminoid matters, the soluble constituents of the ash, &c. Notable traces of soluble starch may sometimes be present, if the mashing has been imperfectly or hurriedly conducted.

634. In brewing, the relative proportion of maltose and dextrin in the wort is of great importance, and is liable to considerable variation, being dependent on the temperature at which the mashing was conducted, the length of time occupied in the

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[1] The divisor given in the text is that generally adopted, and is in accordance with the published tables showing the proportion of dry extract in malt-worts of various densities. Dr Charles Graham, who has had great experience in the analysis of malt-products, informs the author that he employs the division 3·75. Hence, according to him, standard wort of 1057 specific gravity contains 15·2 instead of 14·8 grammes of extract per 100 c.c. O'Sullivan, on the other hand, considers the divisor 3·95 to be more accurate.

[2] Of those commonly used, Baumé's hydrometer is described in par. 11, and the saccharometers of Balling and Brix in par. 493.

process, and the diastasic activity of the malt employed. To a minor extent the proportion will be affected by the character of the water employed for mashing. The composition of the wort largely influences the subsequent fermentation, as a wort containing little dextrin will produce a beer of low density which will clarify readily, but be "thin," and apparently much weaker than beer of the same original gravity but higher final attenuation.

635. C. Graham estimates the maltose and dextrin in beer-worts from the cupric oxide reducing power of the solution before and after inversion. For the estimation of the maltose, the density of the solution is carefully ascertained, and 10 c.c. accurately measured with a pipette and diluted to 100 c.c. This will give a convenient strength of solution for the volumetric estimation by Fehling's solution, but, if anything better than approximate results be desired, it is preferable to use the copper solution gravimetrically, as described in par. 537. 20 c.c. of the diluted wort will be a suitable quantity to employ for the reaction with 30 c.c. of Fehling's solution. The weight of cupric oxide obtained, multiplied by 0·7314, gives the amount of maltose in the quantity of diluted wort employed. Or, if the percentage of maltose contained in the solid extract of the wort be desired, it may be calculated from the following formula:—

$$\frac{\text{Weight of CuO obtained} \times 28232}{\text{Volume in c.c. of undiluted wort employed} \times (\text{density of undiluted wort} - 1000)} = \left\{\begin{array}{l}\text{Percentage of}\\ \text{maltose in solid}\\ \text{extract of wort.}\end{array}\right.$$

The maltose having been determined, 10 c.c. of the wort is mixed with 3 c.c. of sulphuric acid, diluted to 100 c.c., and inverted by heating to 100° C. for three or four hours, in a flask furnished with a long tube (par. 508). The volume of the solution is verified, and, if necessary, the measure is again made up to 100 c.c., when 10 c.c. are carefully measured or weighed, neutralised with sodium carbonate, and the reducing power determined by heating with Fehling's solution *in the same way as before.* The increased reducing power will be due to the dextrose produced from the dextrin of the original wort, due allowance being made for the increased weight caused by the inversion, and to the greater reducing power of the dextrose into which the maltose was converted. If the foregoing directions have been followed, the dextrin may be found by the following rule:—Multiply half the weight of CuO obtained by the action of Fehling's solution on 2 c.c. of the original wort by 1·72 and subtract the product from the CuO obtained from the inverted solution (= 1 c.c. of original). The difference multiplied by 40·8 gives the grammes of dextrin in 100 c.c. of the original wort. If the total solid extract be calculated from the specific gravity of the wort, the percentage of dextrin therein can be readily ascertained.

636. The percentage of *dextrin* is also deducible from the rotatory action of the infusion on polarised light. The liquid should, if necessary, be decolorised as described in par. 465, and the rotation then carefully observed. In order to ascertain how much of the observed effect is produced by dextrin, the rotation due to the maltose present is first calculated. The number of grammes of maltose in 100 c.c. of the infusion having been ascertained by precipitation with Fehling's solution, the figure thus found is multiplied by 2·78, when the product is the circular rotation due to the maltose of the wort. The figure thus obtained, if deducted from the total circular rotation observed, gives the rotation due to dextrin. The angle found, divided by 3·86, or multiplied by ·259, gives the grammes of dextrin in 100 c.c. of the solution. These instructions are based on the assumption that the polarimeter is one in which monochromatic light is employed, and that the infusion is observed in a tube 2 decimetres in length. By dividing the grammes per 100 c.c. by the density of the infusion (water = 1) the actual percentage by weight of the maltose and dextrin in the infusion will be ascertained.

637. J. West Knights (*Analyst*, vii. 211) has described a very simple and rapid method of approximately determining the dextrin in beer-worts. 10 c.c. measure of wort is treated in a small tared beaker with 50 c.c. of methylated spirit of 830 specific gravity. This causes the precipitation of the greater part of the dextrin, which after a few hours collects on the bottom of the beaker as a gummy mass, from which the alcoholic liquid can be readily poured off. The deposit is rinsed with a little more spirit, and the beaker dried in the water-oven and weighed. To the weight obtained an addition of 0·045 gramme is made, as a correction for the dextrin retained in solution by the spirituous liquid. The results are said to be very good.

638. An alternative method of roughly assaying beer-worts for dextrin is also due to Mr West Knights. It is based on the fact that when wort is dialysed for twenty-four hours in contact with an equal measure of water, the diffusion of the sugar is practically complete, whilst a mere trace of dextrin passes through the diaphragm. A glass dialyser 5 inches in diameter should be employed, and the diaphragm should be French gut-skin fastened to the dialyser by an elastic band. 100 c.c. of the wort should be placed in the dialyser, which is suspended in a vessel containing 100 c.c. of water, so as just to touch the surface of the liquid. By this

arrangement there is a slight flow of water from the colloid liquid to the diffusate, so that at the end of the twenty-four hours the volumes of the two liquids can be exactly equalised by pouring some of the water into the wort. At the conclusion of the process, the colloid solution and the diffusate contain equal quantities of maltose, so that the excess of density of the former is due to dextrin and a small quantity of albuminous matter. Thus, if the volumes of the dialysed wort and diffusate be both restored to 100 c.c. by pouring some of the latter into the former, and the density of the diffusate is 1065·5, while that of the colloid solution is only 1042·0, the difference, 23·5, is due to "colloid matter," or, in other words, to dextrin, indefinite carbohydrates, and soluble albuminoids. The number 23·5 divided by 3·85, or multiplied by ·2597, gives the grammes of dextrin, &c., per 100 c.c.[1] The proportion of maltose in the wort may be calculated similarly from the density of the diffusate, the result being multiplied by 2. The results are stated to agree fairly with those obtained by Fehling's solution.

The foregoing method is likely to prove valuable to brewers, as it involves a minimum of manipulation, and does not necessitate the use of a balance. A urinometer, or other delicate hydrometer, may be employed to take the densities.

639. The other constituents of malt-worts which sometimes require to be determined are the *mineral matters*, *free acid*, and *soluble albuminoids*. The acid may be determined as in malt, the ash after evaporating the infusion to dryness, and the albuminoids by distillation with alkaline permanganate as described in par. 623.

640. *Alcohol* is not present in fresh malt-infusion. After fermentation it exists in quantity, being derived chiefly from the splitting up of the maltose (par. 168). The change is accompanied by "attenuation," or reduction in the density of the wort, and it is often desired to ascertain the extent to which this has occurred. This may be effected in the manner described in par. 227.

641. MALT-EXTRACT.

A solid extract of malt is now produced extensively by evaporating an infusion of malt at a low temperature, and generally *in vacuo*. The diastasic power varies greatly according to the care exercised in the preparation.

Malt-extract should be light in colour; dark preparations have been overheated, and hence usually contain no active diastase or soluble albumin, being comparable simply with molasses. The taste should be peculiar and sweet; and the odour pleasant, like that of new bread. The solution in nine parts by weight of water should be only slightly turbid, should filter readily, and should give an abundant precipitate a few minutes after being mixed with an equal measure of a cold aqueous solution of picric acid. The matter insoluble in water should appear under the microscope to consist of amorphous coagulated matter, ferment-particles, and long hexagonal prisms.

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[1] See footnote on page 273.

642. *Water* and *Total Solids* may be determined as in molasses (par. 588), but a good and rapid method is to calculate the solids from the density of the extract. A known weight of the sample should be diluted with an equal weight of water and the density observed at 17°·5 C. The corresponding weight of solids is then learnt from the table on page 212, and the percentage in the sample will of course be twice this amount. The result so obtained will be from ½ to 2 per cent. below the truth. A more accurate plan consists in dissolving the extract in four times its weight of water, observing the density of the solution at 60° F. (=15°·5 C.), and calculating the solids therefrom by the formula :—

$$\frac{(\text{Density of solution} - 1000) \times 1{\cdot}3}{\text{Density of solution.}} = \text{percentage of solids.}$$

The proportion of solids in malt-extract ought not to be below 75 per cent., as diastase does not keep well in less concentrated extracts, though in commercial preparations the solids range from 81 to 14 per cent. The very aqueous samples occasionally contain alcohol. Preparations containing much water often receive an addition of *salicylic acid.* Such a treatment of malt-extract is very objectionable, as the diastase is rendered inactive thereby. On agitating the diluted extract with ether, the salicylic acid is dissolved, and may be recovered by separating and evaporating the ethereal layer, and recognised by dissolving the resultant residue in water and adding ferric chloride, when a fine violet coloration will be produced if salicylic acid be present.

643. The *free acid* in freshly prepared malt-extract is almost entirely lactic acid, but other acids are formed on keeping. The free acid may be determined by dissolving 10 grammes of the sample in 100 c.c. of water and titrating the liquid with decinormal soda, of which each c.c. neutralised represents 0·090 per cent. of lactic acid. The acid should not exceed 0·75 per cent. at the outside, or the diastasic strength of the extract will rapidly disappear.

644. The *diastasic power* is the feature of greatest importance in malt-extract. Methods for the determination of this have been devised by Dunstan and Dimmock (*Pharm. Jour.*, [3] ix. 733–735), and by C. Jungk (*Pharm. Jour.* [3] xiv. 105). The former

process consists in allowing a standard solution of malt-extract to act on a certain quantity of gelatinised starch for a definite time, the termination of the reaction being indicated by iodine. The following method of using the process will be found to be most convenient for ordinary use:—The solution of malt-extract is prepared by dissolving 5 grammes of the sample in 100 c.c. of water. 0·5 gramme of starch (dried at 100° C. before weighing) is gelatinised by boiling with water, and the cold liquid diluted to 100 c.c. The standard solution of malt-extract is then added to 20 c.c. of this mucilage by instalments of 1 c.c., at intervals of half an hour, until it ceases to give any colour, when a small quantity is tested with a dilute solution of iodine. If less than 1 c.c. of the solution produces this effect, more of the mucilage should be added and the operation continued. The process may be hastened by carrying on, in the first instance, more than one experiment with different quantities of malt-extract, in which way a rough idea is obtained of the quantity required, and the exact amount can be readily determined by further experiment.

The process may also be employed to determine the diastasic power of malt. 5 grammes of very finely powdered malt are digested and agitated for one hour with 50 c.c. of cold water. The liquid is then strained off and the residue again digested for an hour with 50 c.c. of water. The liquids are then mixed, made up to 100 c.c., and the solution then allowed to act on starch mucilage in the manner already described. The results indicate the quantity of malt or malt-extract required to convert a certain amount of dry starch.[1]

645. T. S. Dymond (*Pharm. Jour.*, [3] xv. 236) has examined the processes of Dunstan and Dimmock and of C. Jungk. The latter he considers to be untrustworthy, but states that the former gives accurate and constant results, and has proposed the following modification of it, which will be found useful in cases where an approximate idea of the strength of commercial malt-extract is required:—A mucilage of starch is prepared by adding 0·1 gramme of dried starch to 100 c.c. of water, and raising the liquid to the boiling point. This is cooled and mixed with a solution of 1·5 gramme of the sample of malt-extract in 15 c.c. of water. The mixture is raised to 60° C., and tested from time to time by removing sample-quantities of 5 c.c. each, cooling them, and adding two drops of a solution of iodine. The colour is compared with 5 c.c. of a similar mixture, to which iodine but no starch has been added. When the iodine

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[1] For this modification of the published process, the author is indebted to a private communication from Mr Dunstan.

produces no further reaction, the conversion of the starch by the diastase is at an end. With a very good extract this will occur within half an hour, but many commercial extracts continue to react with iodine for nearly three hours. If the conversion is not complete after that length of time, the extract should be condemned, as it is practically useless for its intended purpose, having probably been evaporated at such a temperature as partially or wholly to destroy the diastase. Such samples differ little in dietetic value from honey and other saccharine preparations. The process may be rendered quantitative by accurately noting the time required by different malt-extracts to effect the conversion of the starch, the diastasic strength being inversely proportional to the duration of the reaction.

646. MILK-SUGAR.

Lactose. Lacton. Lactin. $C_{12}H_{22}O_{11}$.

French—Sucre de Lait. *German*—Milchzucker.

(See also Table on page 192.)

This species of sugar is met with only in the milk of the mammalia, herbivorous animals secreting a larger proportion than the carnivora. Lactose is the most constant constituent of milk, from 5 to 6 per cent. being present in human milk and 4 to 5 per cent. in the milk of most of the herbivora.

647. Milk-sugar is usually prepared by curdling milk with rennet or sour whey, removing the coagulum, and evaporating the whey to a thin syrup. The crystals, which gradually separate on standing in the cold, are purified by crystallisation from hot water, re-solution, filtration through animal charcoal, and re-crystallisation on strings or pieces of wood placed in the solution.[1] The product may be further purified by re-solution in water and precipitation from the solution by addition of alcohol, in which milk-sugar is but little soluble.

648. Milk-sugar crystallises in hard, white, semi-transparent, hemihedral rhombic (or trimetric?) prisms or saccharoid masses of the composition, $C_{12}H_{22}O_{11}+H_2O$.[2] The crystals are unaltered at 100° C., but are rendered anhydrous with some difficulty by heating to 130° C. On evaporating a solution of milk-sugar with sand so that the residue forms a thin layer, the anhydrous sugar is often

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[1] For an interesting paper on the manufacture of milk-sugar in Switzerland, by J. Kunz, see the *Pharm. Jour.*, [3] xv. 443.

[2] On rapidly boiling down a solution of milk-sugar in a metallic dish, the solution suddenly solidifies to a porous mass of small anhydrous crystals. These are readily soluble in water, giving a solution rotating $+52°\cdot7$.

obtained. Anhydrous milk-sugar is not further altered at 150° C., but at 170 to 180 it turns brown and yields lacto-caramel, with the loss of the elements of water.

649. A freshly-prepared saturated solution of milk-sugar in cold water contains 14·55 per cent. of the crystallised sugar, but after standing (or immediately on boiling), the solution is found to contain 21·64 per cent., or half as much more. This change in solubility appears to be related to the size of the molecules, for the specific rotatory power of the two modifications of sugar which may be assumed to exist in the solutions is in inverse proportion to the solubility in water.[1] Thus a freshly-prepared solution is supposed to contain the α modification, and a solution which has been kept the β variety. The value of S_D for the α variety is +80°, and for the β kind +52°·7 for a concentration of 12 per cent., and 53°·2 in solutions of 3 per cent.[1] As the latter modification is more soluble than the former, in the proportion of about 3 to 2, it follows that saturated solutions of either modification will exert the same angular rotation on a ray of polarised light.[2]

The figure +52·7 corresponds to a value of $S_D = +55{\cdot}8$ for anhydrous milk-sugar.

650. When boiled with dilute sulphuric acid, milk-sugar undergoes hydrolysis with formation of dextrose and galactose. (see par. 685).

According to Bouchardat (*Ann. Chem. Phys.*, [4] xxvii. 75), milk-sugar is not affected when heated in solution to 100° with oxalic acid; a reaction by which it may be distinguished from cane-sugar, which undergoes inversion (and consequent change in optical activity and reducing power) under the same conditions. On the contrary, Stokes and Bodmer find that oxalic acid is not without invertive influence on milk-sugar, but that citric acid has no action on it, while readily inverting cane sugar. Milk-sugar is stated to be soluble in "distilled vinegar," and to crystallise from the solution unaltered.

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[1] H. W. Wiley has recently reviewed the determinations of the specific rotation of milk-sugar, and considers +52°·5 the most correct figure (*Amer. Chem. Jour.*, vi., No. 5).

[2] Hesse explains this curious fact in the following manner:—The "rotatory powers of the two modifications (of milk-sugar) stand to one another as 3 to 2, consequently in inverse proportion to the solubility of the two forms. A freshly-prepared solution of milk-sugar saturated at 10° C. contains, in 100 parts, 14·55 parts of sugar. In these proportions the molecules of sugar fill the given space so perfectly that any further molecules of sugar added to the solution find no room to dissolve. By boiling or standing there results a contraction in the building up of the molecules, so that the volume of each is reduced to two-thirds of its original expansion. The solution is then only two-thirds full, so that a further one-third part of substance in the same condition may find place in it. A light ray which passes through the volume of the first form must travel a path one-half longer than when it passes through the β form, and, correspondingly, in the first case it is more strongly affected by one-half than in the latter."

651. Milk-sugar does not readily enter into fermentation with yeast alone, but in contact with putrefying casein, as in old milk, it readily ferments, the chief products in this case being alcohol and lactic acid, and the milk-sugar not undergoing previous inversion. *Koumiss* is a product of the fermentation of lactose as existing in mares' milk.

652. Milk-sugar readily becomes brown when heated with alkalies. It forms more or less well-defined compounds with metallic oxides, the neutral lime-compound being soluble, and the basic insoluble. With chloride of sodium, milk-sugar does not appear to form any definite compound.

653. Milk-sugar exhibits a reducing power resembling that of the glucoses rather than cane-sugar. It rapidly reduces the ammonio-nitrate of silver, and this reaction is employed for silvering glass.

654. Determination of Milk-Sugar.

Practically, the estimation of milk-sugar is required simply in milk and products, such as whey and koumiss, derived therefrom.

A method which affords an approximate estimation of the sugar in milk consists in adding a few drops of acetic acid and warming, filtering from the resultant curd, boiling, evaporating the clear whey to a small bulk, again filtering, and then evaporating the filtrate to dryness. The residue, after drying at 130° C. consists almost wholly of milk-sugar and salts. The amount of the former substance present may be ascertained by igniting the weighed residue and noting the loss of weight.

655. Milk-sugar may be estimated by observing the optical activity of its solution. To apply this method to milk, from 61·67 to 70·27 grammes of the sample should be weighed out, 5 c.c. of the solution of lead acetate employed for clarifying sugar solutions (see foot-note on page 201) added, the mixture well shaken, diluted to 100 c.c. with cold water, and at once passed through a dry filter.[1] The clear liquid thus obtained is then poured into a 2-decimetre tube and examined in the polarimeter. If 16·350

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[1] If carefully conducted, this treatment produces a clear filtrate which gives no precipitate on boiling. The liquid should on no account be heated before filtering. The method of operating described in the text was communicated to the author by S. P. Sharples, who finds it requires only fifteen minutes for its performance, while the results are very satisfactory.

grammes of cane-sugar be the standard weight intended to be used with the instrument, the most convenient weight of milk to employ is 61·62 grammes (= 60 c.c.), when the saccharimetric indication only requires to be divided by 3 to obtain the grammes hydrated milk-sugar in 100 c.c. of the sample under examination. If 26·048 be the standard weight for the instrument, 65·7 grammes (or 64 c.c.) of milk should be employed, and the saccharimetric indication divided by 2. If the sodium ray be employed, 70·27 grammes of milk weighed out (or 68 c.c. measured), and the observation made in the 2-decimetre tube, each circular degree of rotation corresponds to 1·5 grammes of hydrated milk-sugar in 100 c.c. of the sample. 100 parts of crystallised represent 95 of anhydrous milk-sugar, of which genuine milk shows from 4 to 5 per cent. H. W. Wiley (*Amer. Chem. Jour.*, vi. No. 5) has recently shown that the estimations of milk-sugar in milk by the foregoing process are below the truth, owing to the incomplete removal of the albuminous matters by the lead solution, and the lævo-rotatory power of those left in the liquid. Hence he has proposed to substitute a mercuric solution for that of the basic lead acetate. Two alternative mercurial reagents are prescribed, the simpler of which is prepared by dissolving mercury in twice its weight of nitric acid of 1·42 specific gravity, and diluting the resultant solution with an equal measure of water. 1 c.c. of this reagent is sufficient to precipitate the albuminoids from 60 to 70 c.c. of milk, but a larger proportion can be employed without affecting the results of the subsequent polarisation. Wiley dilutes the solution to 102·4 c.c., the extra volume of 2·4 c.c. being an allowance for the average space occupied by the albuminous precipitate.

656. Fehling's copper solution (par. 530) is readily reduced by milk-sugar on heating, the proportion of copper reacting approximating to the proportion of 7CuO (= 555·8) for $C_{12}H_{22}O_{11}$ (= 342). This ratio corresponds to a reduction of 100 c.c. of copper solution by ·6786 gramme of milk-sugar, a result which is in close accordance with the figure of Soxhlet, ·676, whose method of operating is described in par. 544. The behaviour of milk-sugar with Fehling's solution has been critically examined by Rodewald and Tollens (*Deut. Chem. Ges. Ber.*, xi. 2076), and their conclusions are generally confirmed by Muter (*Analyst*, v. 35), but that chemist indicates in addition certain points by attention to which the method can be further increased in accuracy. According to Muter, constant results cannot be ensured unless the whole liquid be diluted to such a point as to reduce to insignificance the tendency of the alkali to act on the sugar, while the Fehling's solution is employed in sufficient quantity to instantane-

ously perform the whole reaction, and both the sugar and the Fehling's solution are actually boiling when mixed. Under such conditions the proportion of copper reduced is said to be rigidly 7Cu for $C_{12}H_{22}O_{11}$, as stated above.

The experimental details by which the above equivalent may be ensured are as follows:—The solution is diluted with hot water until it does not contain more than 0·1 per cent. of milk-sugar, and the liquid is brought to brisk ebullition in a large beaker. A very slight excess of boiling hot Fehling's solution is then added,[1] and the whole kept boiling for three minutes and allowed to settle. In a few minutes the precipitate will have subsided, so that the slightly blue liquid can be almost wholly poured off. 50 c.c. of boiling water are then poured on the precipitate, the liquid rapidly filtered, and the precipitate washed with boiling water till free from any trace of free alkali. Muter then moistens the precipitate with two drops of petroleum spirit, drys it in a water-oven, and weighs as Cu_2O, but it is evident that any of the alternative methods of after-treatment may be substituted for the direct weighing of the cuprous oxide. Muter's plan involves the necessity of using a weighed filter, which is apt to suffer from the action of the strongly alkaline liquid.

From the number of cubic centimetres of Fehling's solution employed, the weight of milk-sugar in grammes can be found by multiplying by 0·006786. Or, from the weight of copper or copper oxide, the milk-sugar can be deduced by the factors given in par. 538.

In estimating the sugar in milk by Fehling's solution, the liquid should first be curdled by warming with a few drops of acetic acid and the filtrate boiled to coagulate albumin. The liquid is again filtered, and neutralised with soda before adding the copper solution. Stephens and Kingzett estimate the sugar in milk volumetrically without removing the albuminoids (*Analyst*, x. 30).

Stokes and Bodmer have proposed to determine milk-sugar by treating the curdled and filtered milk with Pavy's ammoniacal cupric solution (see par. 539), which, however, they prefer to prepare with 400 c.c. of strong ammonia per litre. The cupric oxide reducing power of hydrated milk-sugar for this solution is 52 per cent. of that of glucose for the same liquid. The reduction of Pavy's solution by milk-sugar requires time, so the process must not be too hurriedly conducted.

657. The estimation of cane-sugar in presence of milk-sugar, which is required in the analytical examination of sweetened

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[1] It is evident that the measure of Fehling's solution required must be approximately ascertained by previous trials.

condensed milk, may be effected by comparing the optical activity of the original liquid (clarified) with that of which has been treated with invertin (par. 563).

Stokes and Bodmer have recently described (*Analyst*, vol. x.) a method of estimating cane-sugar in presence of milk-sugar based on the following principles:—Coagulation of the milk by citric acid, dilution to ten times its original volume, filtration, and titration of a portion of the filtrate with Pavy's ammoniacal cupric solution as already described. To 100 c.c. of the same filtrate 2 grammes of citric acid should be added, the liquid boiled for ten minutes, cooled, neutralised, made up to 200 c.c., and titrated with the cupric solution as before. The difference between the reducing powers of the solutions before and after inversion is due to the glucose derived from the cane sugar present, the milk-sugar not being inverted by boiling with citric acid.

658. In sour milk, the lactose is converted into an equal weight of lactic acid. This may be determined by titration with standard alkali and phenol-phthaleïn, and the amount so found added to the lactose found by Fehling's solution to obtain the quantity of milk-sugar which existed in the fresh milk.

659. GLUCOSES.

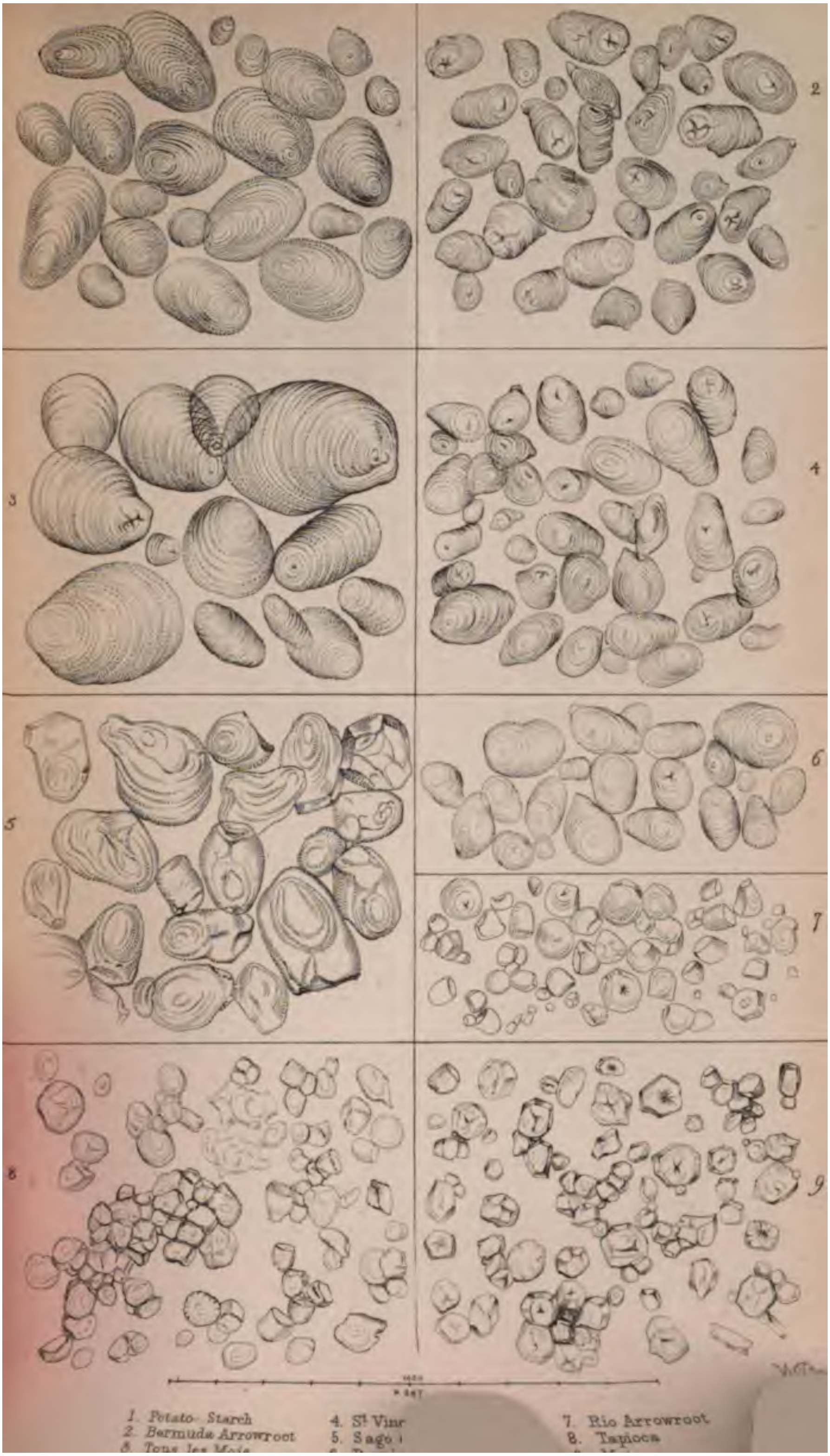
The class of sugars known as glucoses have the composition expressed by the formula $C_6H_{12}O_6$. Their generic and specific characters are described in the tables on page 190 *et seq.*

With the exception of the two species of glucose produced by the inversion of cane sugar, the characters and reactions of which are discussed in the following sections, the glucoses are of little importance.

660. Detection and Determination of Glucoses.

All the principal species of glucose are very similar to each other in their leading chemical properties, though exhibiting differences in certain minor respects and in their physical characters. The chief points of distinction between dextrose and lævulose are stated on page 290, while the description in par. 685 sufficiently characterises galactose. As a class, the glucoses are distinguished from other sugars (1) by not being susceptible of inversion; (2) by the readiness with which they enter into fermentation with yeast, and by the proportion of alcohol yielded by fermentation; (3) by their behaviour with alkalies; and (4) by the readiness with which they undergo oxidation by alkaline solutions of copper. The reduction of a somewhat acid solution of cupric acetate is especially characteristic of the glucoses (compare par. 547).

A number of other liquids besides solutions of copper are reduced



1. Potato Starch
2. Bermuda Arrowroot
3. Tous les Mois

4. S^t^ Vin
5. Sago

7. Rio Arrowroot
8. Tapioca

by the glucoses, and more or less by maltose and milk-sugar also. Thus, in alkaline solution, these sugars reduce blue indigo to white indigo, picric acid to picramic acid, ferricyanides to ferrocyanides, mercuric cyanide and Nessler's solution to metallic mercury, and so forth.

The determination of glucoses is usually based on their reducing action on Fehling's solution, supplemented by observation of the optical activity and specific gravity of their solutions. The details of the methods in which these principles are utilised are fully described in other sections.

661. THE EXAMINATION OF URINE FOR GLUCOSE is of considerable importance, as the presence of dextrose in sensible quantities in the urine is a constant symptom of the disease known as *diabetes mellitus*. Diabetic urine is usually of high density, often reaching 1040, pale in colour, and apt to froth on agitation. Occasionally it is almost a pure solution of dextrose.[1] The proportion of sugar in diabetic urine may be determined approximately by the polarimeter, but the results are deficient in accuracy owing to the presence of other optically active bodies. On the whole, the processes based on the reduction of metallic solutions by the glucose give the best results, the solution most generally employed being that of Fehling. Before applying the test, it is desirable to remove albumin, if present, by heating the slightly acid or acidified urine to boiling, and filtering from any precipitate. The liquid should then be rendered distinctly alkaline by caustic soda or potash, filtered from any precipitate of phosphates, &c., and the copper solution then employed in the following manner :—

Heat to boiling in a test-tube 10 c.c. of Fehling's solution, prepared in the usual way,[2] previously introducing a few small fragments of clay tobacco-pipe to prevent bumping. When boiling, add ½ to 1 c.c. of the urine, previously treated as indicated above. If sugar be abundant, as in a decidedly diabetic urine, a yellowish or brick-red opacity and deposit will be produced. If a negative reaction is obtained, test for traces of sugar by adding 7 c.c. or 8 c.c. of the urine to the hot liquid, heating again to ebullition, and then setting the tube aside for some time. If no turbidity is produced as the mixture cools, the urine is either quite free from sugar, or at any rate contains less than 0·025 per cent. If the quantity of sugar present is small—that is, under

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[1] It is doubtful whether the dextro-glucose contained in diabetic urine is ordinary sucro-dextrose (compare par. 677).

[2] It is absolutely essential that the Fehling's solution used should remain perfectly clear when diluted with its own volume of water, and boiled for a few minutes. If prepared as directed in par. 530, no difficulty will be experienced in this respect.

0·5 per cent.—the precipitation of the yellow or red cuprous oxide does not take place immediately, but occurs as the liquid cools, the appearance being somewhat peculiar. The liquid first loses its transparency, and passes from a clear bluish-green to an opaque, light-greenish colour. This green milky appearance is quite characteristic of dextrose.

By applying the above test quantitatively (see par. 537), the determination of glucose in urine may be readily effected; but it must be borne in mind that traces of glucose are found normally, or at least very commonly, in urine, and hence too great a stress should not be laid on the presence of an insignificant proportion.

662. Pavy's solution (see par. 539) may also be used for the determination of the glucose in diabetic urine, though it cannot be employed for the detection of small quantities of the sugar. Müller and Hagen determine the sugar volumetrically by Knapp's mercurial solution (par. 541), which has the advantage of being applicable to samples of urine containing as little as 0·1 per cent. of glucose, while Fehling's solution cannot be applied quantitatively in the ordinary manner if less than 0·5 per cent. of dextrose be present, owing to the incomplete separation of the cuprous oxide in presence of certain obscure foreign matters contained in urine.[1] Knapp's method has the advantage of being applicable in all cases, and the standard solution undergoes no change on keeping. Albumin should be removed before titration, by heating the urine to boiling, and filtering.

Bodies other than glucose, capable of reducing both Fehling's and Knapp's solutions, are sometimes present in urine, but their exact amount and nature are not known.

663. To render urine fit for the application of Fehling's solution, Carnelutti and Valente recommend that 100 c.c. of the sample should be evaporated to a syrup on the water-bath, 1 c.c. of a 25 per cent. solution of zinc chloride previously mixed with one-fourth of its volume of hydrochloric acid is added, then two volumes of absolute alcohol, and the whole allowed to stand for some hours. The liquid is then filtered, the residue washed with alcohol, the alcohol evaporated from the solution, and the residual liquid made up to 100 c.c. with distilled water. In this solution,

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[1] J. G. Otto recommends that, for titrating solutions containing 1 to ½ per cent. of glucose, the Knapp's solution should be diluted with 4 volumes of water, for those 0·5 to 0·1 per cent. of glucose with 3 volumes of water, while for solutions containing less than 0·1 per cent., 2 volumes of water should be added. In all cases, the urine should be added gradually to the mercurial solution.

excellent estimations of the glucose are said to be obtainable by Fehling's solution.

664. Dextrose. Dextro-glucose. Sucro-dextrose.

French—Sucre de raisin. *German*—Traubenzucker.

This species of sugar, often called simply "glucose," and also known as "starch-sugar," may be produced in various ways, of which the following are the chief:—

a. By the hydrolysis of starch, dextrin, cane sugar (together with lævulose), or some gums, by means of dilute acids, diastase, or invertin.

b. By treating linen rags or similar vegetable matter with sulphuric acid.

c. By decomposing the so-called glucosides (*e.g.*, salicin, gallotannic acid, amygdalin, phloridzin, &c.), by treatment with dilute acids or certain ferments.[1]

665. Dextrose occurs ready-formed, together with lævulose, in honey (see par. 714). It is also said to occur, unmixed with lævulose or cane sugar, in diabetic urine. (See footnote on page 285).

Dextrose is found ready-formed in various fruits, lævulose and cane sugar being also present as a rule. The proportion of dextrose in grapes is as high as 15 per cent.

666. Dextrose usually crystallises from its aqueous solution in granular, hemispherical, warty masses or tabular crystals, containing $C_6H_{12}O_6+H_2O$, but hot concentrated solutions often deposit anhydrous dextrose in prisms. By crystallisation from hot methyl alcohol the anhydrous sugar is obtained in transparent prismatic crystals. The hydrated glucose becomes anhydrous below 100° C. Dextrose melts at 146°, and at about 170° C. loses water and is converted into glucosan, $C_6H_{10}O_5$, and at higher temperatures yields caramel. Dextrose is less soluble than cane sugar in cold water, requiring 1⅓ times its own weight, but it dissolves in all proportions in boiling water, forming a syrup of a sweetening power inferior to a solution of cane sugar,[2] or one of lævulose of the same strength.

667. Considerable discrepancies exist in the determinations of the specific rotatory power of dextrose as ascertained by different

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[1] The dextro-rotatory glucoses obtained by the action of dilute acids on the glucosides are generally assumed to be identical with sucro-dextrose, or grape sugar, but the researches of Hesse and others have thrown considerable doubt upon the accuracy of this view (see par. 677).

[2] According to Behr, three parts of cane sugar possess the same sweetening power as five of dextrose.

observers. In certain cases it is even doubtful whether the recorded numbers apply to anhydrous or to crystallised dextrose. The following table shows the value of S_D and S_j[1] for anhydrous dextrose, according to the observations of various chemists. The figures refer to a solution which has been either heated or kept for some hours, a freshly-prepared solution of dextrose in cold water having a rotatory power about twice as great as that shown in the table. The values printed in prominent type are those obtained by direct observation; the others by calculation, on the assumption that $S_j = S_D \times 1{\cdot}11$. The figures having H. affixed are obtained by calculation from the observed rotation of the *hydrated* dextrose:—

APPARENT SPECIFIC ROTATORY POWER OF β MODIFICATION OF DEXTRO-GLUCOSE IN AQUEOUS SOLUTION, AS DETERMINED BY DIFFERENT OBSERVERS.

Source of Sugar.	Value for Anhydrous Sugar of		Concentration of Solution employed.	Observer.
	S_D or $[\alpha]_D$.	S_j or $[\alpha]_j$.		
Sucrose, . .	+50·5	**+56·0°**	?	Berthelot.
	51·7	**57·4**	?	Béchamp.
	52·9	**58·65**	5–10	Brown&Heron.
	51·9	**57·6**	?	O'Sullivan.
	51·3	**57·0**	?	Schmidt.
Starch, . .	**52·37**	58·13	2¾	Tollens.
	52·74	58·54	10	,,
	52·99	58·82	17½	,,
	52·84	58·65	?	Soxhlet.
	52·70	58·50	10	Salomon.
Diabetic urine,	56·4	62·6	4·5–26	Hoppe-Seyler.
Starch, . .	51·67	57·3	3	Hesse.
	51·51 (H.)	52·2	12	,,
Grapes, . .	52·16	57·9	3	,,
	51·80	57·5	?	,,
Honey, . .	50·97 (H.)	56·6	12	,,
	51·7	57·3	?	,,
Salicin, . .	51·8	57·4	2½–12	,,
	52·4 (H.)	58·2	12	,,
Amygdalin, .	54·2 (H.)	60·1	2	,,
Phloridzin, .	43·7 (H.)	48·5	6	,,

It will be seen from these results that it is very doubtful whether the dextro-glucoses obtained from diabetic urine and from some of the glucosides (*e.g.*, phloridzin) are identical with the sucro-dextrose from starch, honey, or grapes. Even then there is considerable variation in the values of different observers, possibly owing to certain of the observations having been made on freshly-prepared solutions. For practical purposes, the value of S_D for anhydrous dextrose may be taken at $+52^\circ{\cdot}7$, which, multiplied by 1·110, gives $+58{\cdot}5$ as the value of S_j.[1]

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[1] For an explanation of these symbols, see par. 60.

668. Dextrose is not affected by heating for a moderate time with dilute acids. Prolonged treatment is said to result in the formation of products having the probable formula $C_6H_{14}O_7$.

If dextrose be heated with a solution of caustic alkali the liquid rapidly acquires a yellow or brown colour, and on continued heating a humus-like substance separates.

A solution of dextrose dissolves the alkaline earths, forming yellow solutions precipitated by alcohol. By boiling with excess of lime dextrose is rapidly acted on and destroyed.

The action of alkalies and alkaline earths on dextrose is described more fully in par. 522.

Dextrose, when pure, is not precipitated by neutral or basic lead acetate, but gives a white precipitate with an ammoniacal solution of normal lead acetate.

The reaction of dextrose with alkaline solutions of copper and other reducible metallic solutions is described in par. 527 *et seq.*

When heated with oxide of silver and water, dextrose yields glycollic, oxalic, and carbonic acids, but not acetic acid.

By the action of nascent hydrogen dextrose is converted into mannite or mannitol, $C_6H_{14}O_6$.

When quite pure, dextrose is not readily charred by concentrated sulphuric acid, but combines with it to form an acid-ethereal salt, decomposed by water.

With tartaric, benzoic, stearic, butyric, acetic, and other organic acids, dextrose combines to form oily or amorphous solid products, sparingly soluble in water, but dissolved by alcohol and ether.

Other properties and reactions of dextrose are described in the tables on pages 190 and 234. The reactions which distinguish dextrose from lævulose are given in par. 680.

669. **Lævulose. Sucro-lævulose. Lævo-glucose.**

French.—Lévulose. Chyliarose. *German.*—Linksfruchtzucker.

This species of glucose, often called "fruit-sugar," occurs together with dextrose in honey, and many fruits. A variety of lævulose is produced by the action of dilute acids on inulin, which is probably identical with sucro-lævulose. Lævulose is obtained, together with an equal weight of dextrose, by the action of dilute acids, diastase, or invertin on cane sugar. Lævulose is not a product of the action of dilute acids on any known glucoside.

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[1] Tollens (*Ber.*, xvii. 2234) gives the following formula for calculating the specific rotation of dextrose in solution :—$S_D = 52^\circ{\cdot}50 + 0{\cdot}018796c + 0{\cdot}00051683c^2$.

When cane sugar is heated to 165°–170° C. for some time it is converted without change of weight into a mixture of dextrose and lævulosan, $C_6H_{10}O_5$. On dissolving the product in water and treating the solution with yeast, the dextrose ferments and the unfermentable lævulosan remains, and can be converted into lævulose by boiling with dilute acid.

670. The principal physical and chemical properties of lævulose are described on p. 190. It presents a close general resemblance to dextrose, the following being the chief differences of analytical value:—

a. Lævulose is not readily crystallisable (*Comp. rend.*, xciii. 547), and is more soluble in alcohol than dextrose.

b. The aqueous solution of lævulose is much sweeter than one of dextrose, and somewhat sweeter than one of cane sugar of the same strength.

c. Mixed in ice-cold 5 per cent. solution with 120 per cent. of its weight of fine-powdered slaked lime (which should be added gradually, the vessel being immersed in ice-cold water), a milky liquid is obtained, which gradually becomes pasty from the formation of a difficultly-soluble calcium lævulosate, $CaO,C_6H_{12}O_6,H_2O$, while dextrose on similar treatment yields a freely soluble compound,[1] which can be separated by filtration through linen. The residue, after being washed and strongly pressed, may be suspended in water and decomposed by oxalic or carbonic acid, when a solution of pure lævulose is obtained, which yields *anhydrous* lævulose by evaporation *in vacuo* over sulphuric acid.

d. The respective reducing actions of dextrose and lævulose on Fehling's copper solution are usually assumed to be identical. According to Soxhlet, however, the reducing action of the former is sensibly greater than that of the latter (see par. 545). Allihn states that the reducing action of dextrose and lævulose are identical if care be taken to continue the boiling of the solution for half an hour.

e. The reducing action of dextrose on Knapp's mercurial solution is sensibly the same as that of lævulose, but the latter glucose exerts a far stronger reducing action on the solution of Sachsse, equal amounts of the dextrose and lævulose reducing 100 and 148·6 c.c. of Sachsse's solution respectively (see par. 543).

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[1] If invert sugar or honey is to be treated for lævulose, the proportions of lime and water must be modified accordingly : 10 parts of invert sugar, 6 of slaked lime, and 100 of water are then the right proportions.

f. When a solution of dextrose is heated with bromine water, and the liquid then treated with silver oxide (care being taken to avoid excess of the latter), gluconic acid, $HC_6H_{11}O_7$, is formed, which may be obtained as a syrup on evaporation. If slaked lime be added in excess to its lukewarm solution, and the liquid filtered and heated to boiling, the acid is almost completely precipitated as a basic calcium gluconate. When lævulose is similarly treated with bromine water and oxide of silver it yields glycollic acid, $HC_2H_3O_3$, the calcium salt of which crystallises in silky needles, which are more soluble in hot water than in cold. Digestion with excess of argentic oxide converts gluconic into glycollic acid.

g. The specific rotatory power of lævulose is −98°·8 for the D line at 15° C., decreasing by 0·6385 degree for each increase of 1° C. in the temperature. At 87°·2 C., the rotation is −52°·7, being equal to that of dextrose at the same temperature, but in the opposite direction.

671. The change in the optical activity of lævulose by increase of temperature affords a means of determining it in the presence of other sugars. For this purpose, the solution, previously clarified, if necessary, and not too dilute, is carefully neutralised, and the rotatory power observed in a tube round which a current of very cold water is caused to circulate by an arrangement similar to that of a Liebig's condenser, having an orifice for the insertion of a thermometer. The rotation and temperature having been noted, a current of hot water is passed round the tube until a constant temperature is attained, when the rotation and temperature are again observed. If an instrument employing sodium-light has been used and the observation made in a 2-decimetre tube, the number of grammes of lævulose in 100 c.c. of the solution may be found by the following rule:—Subtract the temperature of the cold water observation from that of the hot water; multiply the difference, expressed in centigrade degrees, by 1·277; then the product divided into 100 times the change in rotation by increase of temperature (expressed in circular degrees) gives the number of grammes of lævulose in 100 c.c. of the solution.[1]

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[1] Suppose that the solution at 4° C. caused a rotation of −19·0 circular degrees; and at 96° C., the circular rotation was −10°·5. The difference of temperature is 92° C. and that in optical activity 8°·5. Then by the rule given in the text:—$\frac{8·5 \times 100}{92 \times 1·277} = \frac{850}{117·484} = 7·24$ grammes lævulose per 100 c.c.

672. Invert Sugar.

French—Sucre interverti. *German*—Krümel-sucker.

Invert sugar exists largely in honey, molasses, and many fruits. It is a mixture of equivalent proportions of dextrose and lævulose, produced by the action of heat, diastase, acids, salts, or other agents on cane sugar and some of its isomers.[1] The conditions most favourable for its formation have been already described (par. 502 *et seq.*)

673. Invert sugar is an uncrystallisable syrup having a sweeter taste than cane sugar. In its chemical reactions and optical properties it behaves strictly as a mixture of dextrose and lævulose.

By treatment with lime, in the manner described in par. 680, the dextrose and lævulose of invert sugar may be partially separated. Lævulose is less readily fermentable than dextrose, and hence when a solution of moist sugar is treated with yeast, the dextrose disappears first.

674. Invert sugar is now made largely for brewers' use, being sold under the names of "invert" or "inverse sugar," "saccharum," "malt-saccharum," &c. Starch sugar and cane sugar are often added. The analysis of such products may be effected in the same manner as that of honey (see par. 725), but it is generally sufficient to estimate the sugar by Fehling's solution before and after inversion. These estimations give the data for calculating the cane or uninverted sugar of the sample and the total glucose, without distinguishing between the dextrose and lævulose.

675. Galactose. Lactose.[2]

When milk sugar is heated with dilute sulphuric or, preferably, hydrochloric acid, it undergoes hydrolysis, the rotatory power of the solution increasing from 52·7 to 67·5. The product of the reaction is frequently stated to be lactose or galactose, but it is now definitely proved that the action of dilute acid on milk sugar really results in the formation of two isomeric glucoses, corresponding with sucro-dextrose and sucro-lævulose. In the case of milk sugar, however, both of the resultant glucoses are dextro-rotatory, and their freshly-prepared solutions exert a stronger dextro-rotatory power than after standing or heating. The complete separation of the two glucoses is difficult to effect, but one of them has been satisfactorily identified with sucro-dextrose, while the other, or galactose proper, is characterised by yielding mucic acid instead of saccharic acid on oxidation with nitric acid (par. 496 *et seq.*).

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[1] Maumené regards ordinary invert sugar as a mixture of dextrose, lævulose, and an optically inactive sugar, the composition varying with the conditions of the inversion.

[2] The name lactose is sometimes applied to milk-sugar itself, as well as to the glucose resulting from its hydrolysis, a practice which has caused some confusion.

676. Galactose is less sweet than cane sugar. By reduction with sodium amalgam it yields dulcite, whilst by heating with bromine water it is converted into lactonic acid, $C_6H_{10}O_6$, which forms deliquescent crystals, and yields, when warmed with excess of lime, a basic salt, which separates on heating the filtered liquid to boiling (compare par. 670, *f.*).

677. A Rindell states the specific rotatory power of galactose in 10 per cent. solution at 15° C. to be $+ 81{\cdot}27$ for the sodium ray, and for calculating the rotation for other temperatures and concentrations gives the following formula :—$S_D = +83{\cdot}037 + 0{\cdot}199c - (0{\cdot}276 - {\cdot}0025c)t$. The mean of this value $(+81{\cdot}27)$ and the number for dextrose (52·7) gives 66·98 as the calculated rotation for inverted (hydrated) milk sugar against 67·50 actually found.

678. **Commercial Glucose. Starch Sugar.**

Under the names of glucose, saccharum, grape sugar, starch sugar, and other more fanciful cognomens, are manufactured and sold a variety of starch-products in which dextrose is the leading constituent. Commercial glucoses are employed by brewers as substitutes for malt and cane sugar, by vinegar-makers, and large quantities are used by manufacturers of fancy-sugars, sweetmeats, and preserves. Table-syrups are also manufactured from starch glucose, and honey is extensively adulterated with it. In America, coffee-sugar is largely mixed with glucose, and the same sophistication has recently been practised in this country. Starch glucose is likewise used for the manufacture of factitious wine.

679. Commercial starch glucose is produced by the action of dilute acid on starch or starchy matter, or occasionally woody fibre. In America it appears to be wholly made from maize starch, but in Europe rice and potato starch are frequently used.[1]

As a rule, sulphuric acid is used as the converting agent, the proportion employed ranging in practice from 1 to 3 per cent., according to the kind of product desired and the details of the subsequent manipulation. The starch, or amylaceous substance, is either boiled with the acid and water in an open tank, or heated with it in strong copper cylinders under high pressure. If the first method be adopted, and the process arrested as soon as a cold sample of the liquid ceases to give a blue colour with iodine, the product contains a large proportion of dextrin; but if high pressure be employed, and the action pushed further, dextrose is the chief product. In either mode of operating, maltose and, very commonly, other products are formed in addition to dextrose and dextrin. The acid is next neutralised by addition of chalk or ground marble, milk of lime being added to remove the last traces, the resultant gypsum allowed to settle, the liquid decolorised, if necessary, by animal charcoal, and evaporated *in vacuo* till it acquires a density of 1400 to 1420.

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[1] It is not certain that the products thus obtained are strictly identical with those from maize starch. J. Frankel has published (through H. C. Baird & Co., Philadelphia) *A Practical Treatise on the Manufacture of Starch Sugar*, based on the German of L. von Wagner.

680. Oxalic acid is said to be substituted for sulphuric acid by certain firms, the resultant calcium oxalate being more insoluble than calcium sulphate.[1] A small quantity of hydrochloric acid appears to be employed in a few cases.

681. Starch glucose occurs in commerce in several forms, varying from the condition of pure anhydrous dextrose, through inferior kinds of solid sugar, to the condition of a thick syrupy liquid resembling glycerin, which contains a large proportion of dextrin.[2]

682. A great number of so-called analyses of commercial starch sugars have been published, but the majority are vitiated by the employment of faulty methods of analysis, or by an insufficient knowledge of the constituents of starch sugar. Thus, many analysts give only the proportions of dextrin and dextrose, the latter being deduced from the cupric oxide reducing power of the sample. Such a mode of expression is gravely in error in many cases, since it ignores the presence of maltose, which is a very important and common, if not a constant, constituent of products obtained by the action of dilute acids on starch.[3] Again, many

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[1] When the conversion is affected by sulphuric acid, the glucose solution retains a considerable quantity of dissolved calcium sulphate. More complete separation occurs on concentrating the liquid to a density of about 1240, and a further deposition ensues when the sugar is fermented. The calcium sulphate may be very completely removed by treating the glucose solution with barium oxalate.

[2] In America, the term "glucose" is restricted to the syrupy preparations, the solid products being distinguished as "grape sugar." The following grades are recognised :—

Liquid Varieties.—Glucose, mixing glucose, mixing syrup, corn syrup, jelly glucose, and confectioners' crystal glucose.

Solid Varieties.—Solid grape sugar, clipped grape sugar, granulated grape sugar, powdered grape sugar, confectioners' grape sugar, brewers' grape sugar.

[3] Although the total *percentage* of matter useful to the brewer is the same whether a commercial glucose consist wholly of dextrose or in large part of

specimens of starch glucose contain a notable percentage of unfermentable carbohydrates, apparently produced by over-treatment with acid, and to which the formula $C_6H_{14}O_7$ has been attributed, but certain of which appear to be identical with the body recently described by Schmitt and Coblenzl (*Ber.*, xvii. 1000, 2456; *Jour. Chem. Soc.*, xlvi. 981, xlviii. 134), under the name of gallisin.

683. GALLISIN was prepared by fermenting a 20 per cent. solution of starch sugar with yeast at 18° to 20° C. for five or six days. The resultant liquid was filtered, evaporated to a syrup at 100°, and shaken with a large excess of absolute alcohol. The syrup thickened but did not mix with the alcohol. The alcohol was poured off, and the residue shaken with a fresh quantity, and by repeating this process the unaltered sugar and other impurities were removed, the syrup being converted into a crumbling yellowish grey mass, which by pounding in a mortar with a mixture of equal parts of alcohol and ether was obtained as a gray powder. It was purified by solution in water, boiling with freshly-ignited animal charcoal, filtering, evaporating to a syrup, and repeating the treatment with alcohol and ether. The product was dried over sulphuric acid. Thus obtained, gallisin is a white, amorphous, extremely hygroscopic powder. Its taste is at first slightly sweet, but after a time becomes insipid. Gallisin is readily decomposed by heat, giving off water and carbon dioxide even at 100.° It is

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maltose, the *quality* of the material, as measured by the character of the beer produced, is very different, beer brewed from maltose being greatly superior to a *glucose* beer. The latter is apt to be thin and deficient in head, very clean, and of a vinous character. Maltose gives a beer of full body, good head, soft and creamy on the palate. It keeps well, and, owing to the gradual after-fermentation which occurs, continues brisk and sparkling. These remarks apply to beer brewed from acid-made maltose, as well as to malt-brewed beer.

On account of the superiority of maltose over dextrose as a brewing material, it is desirable to limit the action of the dilute acid used for converting the starchy matter. In practice, it is found that a mixture of two parts of maltose and one of dextrin is the most generally suitable for brewers' purposes. This product, which has been introduced under the name of "dextrin-maltose," is obtained if the action of the acid be arrested when the specific rotatory power of the solids has decreased to about +171° for the transition-tint, or +151° for the sodium ray. The value of K for the solid matter should be about 42. The proportion of solids present is ascertained by removing the sulphuric acid by a slight excess of baryta-water and taking the density of the solution (par. 488).

The dextrin of brewers' glucose is of value for giving "body" to the beer. A smaller proportion is required for running ales than for heavier or "stock" ales.

readily soluble in water, nearly insoluble in absolute alcohol, and but slightly more soluble in methyl alcohol, in which respect it differs from dextrose. It dissolves in a boiling mixture of alcohol and glacial acetic acid, but is insoluble in ether, chloroform, or hydrocarbons.

684. Gallisin is stated to have the composition $C_{12}H_{24}O_{10}$. Its concentrated aqueous solution is distinctly acid to litmus, and a sparingly soluble barium compound may be obtained therefrom by adding alcoholic baryta. Gallisin reduces nitrate of silver on heating, especially on addition of ammonia, reduces bichromate and permanganate, and precipitates hot Fehling's solution. Its cupric oxide reducing power is stated to be 45·6. Knapp's mercurial solution is also reduced by gallisin.

685. Gallisin is dextro-rotatory, the value for S_D being stated to be $+80^\circ \cdot 1$ in 27 per cent., $+82^\circ \cdot 3$ in 10 per cent., and $84^\circ \cdot 9$ in 1·6 per cent. solutions.

By heating with dilute sulphuric acid for some hours, gallisin yields a large proportion of dextrose, but its complete conversion has not, so far, been effected.

686. The presence of an unfermentable carbohydrate in starch sugar was long since pointed out by O'Sullivan, and Neubauer has described two such bodies of little reducing power, one of which was soluble in alcohol, and had a dextro-rotatory power of $+78^\circ$, while the other was not dissolved by alcohol, and had a rotation value of $S_D = +93^\circ$.

687. It is doubtful whether "gallisin," as hitherto obtained, is really a definite compound,[1] but the possibility of isolating a reducing or optically active body from the liquid left after fermenting solutions of many specimens of starch sugar cannot be ignored in considering the composition of commercial glucose. It is probable that the proportion of unfermentable matter has been exaggerated, and O'Sullivan states that starch sugar manufactured by the quick-action process, using high pressure, contains very little, if any, of such unfermentable carbohydrates.

688. According to Nessler (*Zeits. Anal. Chem.*, xx. 466), starch

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[1] The value of the researches on gallisin by Schmitt and Coblenzl is discounted by their giving a process for analysing commercial starch sugar in which the cupric oxide reducing power of the sample is assumed to be wholly due to dextrose and gallisin. For all that appears in their researches they might be ignorant of the existence of maltose, though the process employed for the preparation of gallisin would not improbably lead to its contamination with maltose if any of that sugar had escaped fermentation. A mixture of much maltose with a non-reducing substance of comparatively low rotatory power would give values for K and S similar to those attributed to gallisin.

sugar is liable to contain an unfermentable body capable of producing unpleasant symptoms when taken internally. His conclusions have received some confirmation from Schmitz, Kedsie, and others. The subject has been investigated by von Mering, who attributes the results of Schmitz to the enormous quantities employed, and those of Nessler to the fact that he used the unfermentable residues after they had been evaporated to dryness and taken up again with water, whereby they are changed. The United States Committee on Glucose investigated these statements very carefully, and concluded that there was nothing of an injurious nature in the starch sugar manufactured in America, which is derived entirely from maize; but their experiments did not extend to glucose from potatoes, with which the German chemists worked.

H. W. Landbeck has described an unfermentable, poisonous, bitter substance, giving many of the reactions of colchicine, and which he states is sometimes present to a considerable extent in commercial glucose and badly fermented beer (*Pharm. Jour.*, [3] xi. 832).

689. The following analyses of commercial glucoses, quoted by W. G. Valentin (*Jour. Soc. Arts*, xxiv. 404), are amongst the most complete, and probably most reliable, hitherto published:—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Dextrose, ...	80·00	58·85	67·44	63·42	61·46
Maltose, ...	none	14·11	10·96	13·50	13·20
Dextrin, ...	none	1·70	none	none	none
Unfermentable carbohydrates, with a little albuminoids, . .	8·20	9·38	4·30	8·40	8·60
Mineral matter, . .	1·30	1·40	1·60	1·50	1·60
Water, ...	10·50	14·56	15·70	13·18	15·20
	100·00	100·00	100·00	100·00	100·00
Total solid matter, . .	89·50	85·44	84·30	86·82	84·80
Matter of use to the brewer,	80·00	74·66	78·40	76·92	74·60

No. 1 was somewhat brown, very hard, and of English manufacture. No. 2 was pale straw-coloured, softish, French. No. 3, whitish, somewhat hard, English. No. 4, whitish, somewhat hard, German. No. 5, white, somewhat hard, German.

The following analyses are by I. Steiner (*Dingler's Polyt. Jour.*, ccxxxiii. 262):—

	No. 1.	No. 2.	No. 3.	No. 4.
Dextrose, ...	45·40	26·50	76·00	...
Maltose, ...	28·00	40·30	5·00	42·60
Dextrin, ...	9·30	15·90	...	39·80
Unfermentable carbohydrates, ...	1·50	7·00	5·30	8·90
Albuminoïds, . . .	traces	1·80	·20	...
Free acid (as H_2SO_4), .	·08	·03	·05	..
Mineral matter, . .	·30	2·50	·40	1·10
Water, ...	15·50	6·00	13·30	7·60
	100·08	100·03	100·28	100·00
Total solid matter, . .	84·42	93·97	86·65	92·40
Matter of use to the brewer,	82·70	82·70	81·00	82·40

No. 1 was of German origin, white and soft. The other samples were English, and made from maize without previous separation of the starch.

690. These analyses are unusually elaborate, and for commercial purposes there is no occasion to enter so much into detail. Many analysts limit their statements to the proportions of water, ash, dextrin, and glucose, ignoring the maltose altogether. This practice is very objectionable, as, in an analysis so stated, not only is the maltose classed as dextrose, but the amount of dextrin is also seriously in error. Nevertheless, the cupric oxide reducing power of the sample is a character of considerable value for the commercial classification of a glucose or for assaying a sample during the process of conversion, provided its true meaning be not misinterpreted. Taken together with the specific rotatory power of a sample, and the percentage of ash and water, it often affords ample information for commercial purposes.

691. H. W. Wiley (*Proc. Amer. Assoc. Adv. Science*, xxix., xxx.) has obtained by the analysis of thirty-five samples of *glucose syrup* (made by the Peoria Grape Sugar Company, Buffalo), results of which the following is an epitome :[1]—

	Highest.	Lowest.	Average.
Specific gravity, ...	1440[1]	1406	1414·8
K, in terms of dextrose, ...	62·5	39·23	52·89
S_D (Rotation of sample for D line), .	107·99	75·47	92·52

692. Wiley has also determined the change occasioned in the

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[1] The water in the sample of highest density (a heavy confectioners' glucose) was but 6·37 per cent., while a sample of 1409 specific gravity contained 15·40 per cent. of water. The reducing power was lowest in the sample of greatest optical activity, a fall of 1 degree in the value of S_D (calculated on the

optical activity and reducing power of glucose syrup by heating with dilute acid. As a result, he found the value of S_D for the inverted sugar was about +54, the close approximation of which figure to the specific rotation of dextrose =(+52·7) shows that the inversion was nearly complete. The value of K after inversion ranged from 79·00 to 90·10. It is a misfortune that the water in these samples does not appear to have been determined.[1]

693. The *solid varieties* of commercial starch glucose have only about one-half the rotatory power of the syrups, while their reducing power ranges from K=70 to K=87. This is exclusive of the anhydrous crystallised glucose which is now manufactured, a sample of which contained 99·4 of real dextrose and 0·6 per cent. of water.

694. A very useful method of assaying glucose solution in the course of conversion consists in calculating the percentage of total solids in the sample from the solution-density (see par. 488), deducting the reducing power found by Fehling's solution, and calling the difference "dextrin, &c."

695. As already stated, analyses of commercial glucose which ignore the presence of maltose are merely of value for comparative purposes, and do not even approximately show the proportion of the constituents actually present. The dextrose is usually over-stated, and the percentage of dextrin is also seriously in error. This is well shown by the following results obtained by the author from a commercial glucose. Column A. shows the composition on the assumption that all the reducing sugar is glucose, the remaining organic matter being dextrin. Column B. gives a more correct analysis of the material.

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sample) corresponding to a rise of approximately 0·75 per cent. in the value of K. A sample which in 10 per cent. solution showed a rotation of +53 degrees on a cane sugar scale had also a reducing power of K=53, a fall of 1 degree on the sugar scale corresponding to a rise of 1·25 per cent. in the reducing power. In cases in which the density of the syrup differs sensibly from 1041 (corresponding to about 15 per cent. of water), Wiley corrects the cane sugar units before calculating to the reducing power, by subtracting ·003 ($a \times d$) when the density of the sample exceeds 1409, and adding the same amount to the observed sugar-units when the density is less than 1409 ; a signifying the rotation of a 10 per cent. solution in sugar units, and d the difference between 1409 and the density of the sample.

[1] In some cases, the inversion was effected by heating the glucose solution, with 10 per cent. by measure of sulphuric acid of 1·25 specific gravity, to 100° C. for three to six hours. Some of the better results were obtained by increasing the temperature of the bath to 104°, by addition of salt, the heating being continued for three hours.

	A.	B.
Water,	17·77	17·77
Mineral matter,	·63	·63
Dextro-glucose,	72·60	66·32
Maltose, &c.,	...	10·13
Dextrin,	9·00	5·15
	100·00	100·00
Total solid matter,	82·23	82·23

696. The following data, obtained by the analysis of the above sample, illustrate the mode, first suggested by the author, of deducing the relative proportions of dextrose, maltose, and dextrin in such products.

a. On carefully drying the powdered sample, first at about 60° C., and subsequently at 100°, it lost a weight corresponding to 17·77 per cent. of water; leaving 82·23 per cent. of *total solids.*[1]

b. On igniting the dried sample it left 0·63 per cent. of *ash.* Hence the *organic solids* amounted to 81·60 per cent.

c. By Fehling's test (see par. 537) the sample was found to have a *cupric oxide reducing power* ("K") equivalent to 72·6 per cent. of dextrose. The reducing power of maltose may be taken as $\frac{62}{100}$ that of dextrose.

d. A solution containing 20 grammes of the original sample per 100 c.c., observed in a 2-decimetre tube, caused a circular rotation of +23·7° for the sodium line D. Hence the *value of* S_D for the sample was +59°·25.[2]

The values of S_D for dextrose, maltose, and dextrin are respectively +52·7, +139°·2, and +198° (see Dextrin).

If S be the apparent specific rotatory power, K the cupric oxide reducing power of the sample, and O the percentage of organic solids, then the percentage of maltose may be found by the following rule:—Subtract the reducing power (K) from the organic solids (O), and multiply the difference by 198. To the product add 52·7 times the reducing power (K) of the sample. Divide their sum by 100, subtract the resultant figure from the specific rotatory power (S), and divide the remainder by 0·313. The dividend is the percentage of *maltose, &c.*, in the sample.[1]

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[1] As a fact the percentage of total solids in the analysis quoted in the text was deduced from the solution-density, as stated in the first edition. The method of direct determination by drying is substituted in the test as a more accurate method of analysis.

[2] $S_D = \frac{23\cdot7}{2 \times \frac{20}{100}} = 59\cdot25$ (See par. 59).

The percentage of maltose multiplied by 0·62, and the product subtracted from the reducing power (K), gives the percentage of *dextrose* in the sample.

The sum of the maltose and dextrose subtracted from the organic solids gives the percentage of *dextrin, &c.*

Applying these rules to the sample of which the analytical data have been given, the percentages of dextrose, maltose, and dextrin are found to be respectively 66·32, 10·13, and 5·15, together making 81·60.

697. Instead of ascertaining the organic solids directly, they may be deduced from the solution-density of the sample, but in that case it is desirable to subtract twice the percentage of ash from the total solid, and divide the remainder by 3·94 to obtain the percentage of organic solids.[2]

698. In estimating the reducing power by Fehling's solution, the gravimetric method should be employed, and in the manner prescribed in par. 537, as it was in that way the value of K for maltose was determined.

699. In the case of liquid samples, it is preferable to employ 10

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[1] For the sample of which the analytical data are given in the text :—

Total solids, . . 82·23
Ash, . . . ·63
Organic solids (O), 81·60
Reducing power (K), 72·60
Difference, . . 9·00 × 198 = 1782
Reducing power (K), 72·6 × 52·7 = 3826 Specific rotation (S) 59·25
Sum, 5608 ÷ 100 = 56·08
3·17 ÷ ·313 =
10·13 per cent. of maltose.

If m be the percentage of maltose, g the dextro-glucose, and d the dextrin in the sample, then—

$$m = \left(S - \frac{52{\cdot}7K + 198(O - K)}{100}\right) \div 0{\cdot}313$$
$$g = K - 0{\cdot}62m\text{; and}$$
$$d = O - g - m.$$

These formulæ are deducible from the data in the text. A fuller description of the method of calculation was given in the first edition of this work.

[2] H. T. Brown prefers to state the values of S and K on the assumption that the division 3·86 is uniformly correct for ascertaining the concentration of solutions of carbohydrates from the density. Under these conditions, the

grammes instead of 20 grammes per 100 c.c., for the estimation of the rotatory power. The solution of solid samples should be heated to 100 C. for at least ten minutes before use, in order to destroy the tendency of freshly-dissolved dextrose to exercise an abnormal rotatory action.[1]

700. In analysing samples of commercial starch sugar by the foregoing process, the determinations must be made with the *greatest possible care*, as very slight variations in the proportion of solids, and in the values of K and S, correspond to considerable differences in the composition of the sample. This is a serious defect of the method, but another of equal, if not greater, importance is the influence which the presence of other bodies has on the results. Too little is known of these substances, of which "gallisin" is the type, to allow of a definite allowance or correction being made for their presence, yet their disturbing influence on the value of K and S is unquestionable.[2] Hence,

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specific rotations of dextrose, maltose, and dextrin for the transition-tint become respectively +58·6, +150°, and +216°, the value of $K_{3\cdot86}$ for maltose being 61·0.

From these data, H. T. Brown calculates the composition of the sample by the following equations:—

$$g = 438{\cdot}9 - 2{\cdot}03 S_{j_{3\cdot86}} - 2{\cdot}19K\text{; and}$$
$$m = 1{\cdot}64K - 1{\cdot}64g.$$

Using these formulæ for the analysis of a sample of known composition, Mr Brown informs the author that he obtained the following results:—

	Dextrose.	Maltose.	Dextrin.
Actual composition of sample, . .	40·45	41·09	18·45
Found by analysis $\begin{pmatrix} S_{j_{3\cdot86}} = 126{\cdot}19 \\ K_{3\cdot86} = 65{\cdot}82 \end{pmatrix}$.	38·60	44·64	16·76

[1] This "bi-rotatory power" is very marked in many samples of solid starch sugar, but is not noticeable in the syrups. It is not improbably the cause of some of the discordant results obtained by different observers of the specific rotatory power of dextrose (see par. 667).

[2] If a mixture were made of 40 parts each of dextrose and maltose, and 20 of dextrin, the calculated optical activity and reducing power of the product would be:—

	S_D.	K.
40% dextrose at 52·7 and 100, ...	21·08	40
40% maltose at 139·2 and 62, ...	55·68	24·8
20% dextrin at 198 and 0, ...	39·60	0
Characters of the mixture, . . .	116·36	64·8

If 3 per cent. of the dextrin in this mixture were replaced by an equal weight of some non-reducing carbohydrate of one-third the optical activity of dextrin ($S_D = 66$) the calculated value of S_D for such a sample would be such analyses of starch sugar must not be regarded as scientifically correct, though they are very superior to those showing the total reducing powers as dextrose, and stating the remaining carbohydrates as dextrin. The error falls chiefly on the maltose, the determination of which is apt to be seriously below the truth, and in some cases a negative quantity is found.

701. The difficulty may be in great measure avoided by an ingenious process due to H. W. Wiley (*Chem. News*, xlvi. 175), based on the assumption that dextrose and maltose are oxidised to optically inactive products when heated with excess of an alkaline solution of mercuric cyanide, and that dextrin, which is not oxidised thereby, has its optical activity unaffected. The following is the mode of operation adopted by Wiley.

a. The cupric oxide reducing power of the sample is ascertained in the usual way by Fehling's solution.

b. The specific rotatory power is determined by polarising a 10 per cent. solution (previously heated to boiling) in the ordinary manner.

c. 10 c.c. of the solution employed for *b* (= 1 gramme of the original sample) is treated with an excess of an alkaline solution of mercuric cyanide,[1] and the mixture boiled for two or three minutes. It is then cooled and slightly acidulated with hydrochloric acid, which destroys the reddish-brown colour possessed by the alkaline liquid. The solution is then diluted to 50 c.c., and the rotation observed in a tube 4 decimetres in length. The angular rotation

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+ 113°·40, the reducing power being unchanged. But on calculating the composition of such a sample by the rule given in the text it would appear to contain :—

	Per cent.
Dextrose, ...	45·88
Maltose, ...	30·52
Dextrin, ...	23·60
	100·00

This is a very possible case in practice, and hence the method has a tendency to indicate a proportion of maltose considerably below the truth.

[1] The mercuric solution is prepared by dissolving about 120 grammes of mercuric cyanide and the same quantity of caustic soda in 1 litre of water, and filtering the liquid through asbestos. 20 c.c. of this solution should be employed for samples having K less than 65 per cent., and 25 c.c. when the reducing power is greater than this. In all cases care must be taken to use a slight excess of the mercuric solution, which may be ascertained by holding a piece of filter-paper with a drop of the solution on it over fuming hydrochloric acid, and then over sulphide of ammonium or sulphuretted hydrogen water, when a dark stain, due to mercuric sulphide, will appear on the paper.

observed will be due simply to the dextrin, the percentage of which in the sample may be calculated by the following formula :[1]—

$$\frac{\text{Circular rotation} \times 1000 \times \text{volume in c.c. of solution polarised}}{198 \times \text{length of tube in centimetres} \times \text{weight of sample in solution employed for mercury treatment.}} = \text{Percentage of dextrin.}$$

702. The percentages of dextrose and maltose may be deduced from the reducing power of the sample, or from the difference between the specific rotatory power before (S) and after (s) the treatment with the alkaline mercuric solution. Using the same symbols as before, with the addition of u for the unknown and presumed inactive organic matter, the following equations result :—

$$\mathrm{O} = g + m + d + u \text{ ; } \mathrm{K} = 1{\cdot}00\, g + {\cdot}62m$$
$$\mathrm{S} = {\cdot}527g + 139{\cdot}2m + 1{\cdot}98d \text{ ; } s = 1{\cdot}98d.$$

From these data :—

$\mathrm{S} - s = {\cdot}527g + 139{\cdot}2m$; and ${\cdot}527\mathrm{K} = {\cdot}527g + 32674m$; whence $1{\cdot}06526m = \mathrm{S} - s - {\cdot}527\,\mathrm{K}$; $m = \dfrac{\mathrm{S} - s - {\cdot}527\mathrm{K}}{1{\cdot}06526}$

The proportions of dextrose, dextrin, and inactive carbohydrates are deduced by means which are evident.

703. In Wiley's process it is assumed that the indefinite carbohydrates have no optical activity and no reducing action on Fehling's solution. Both these assumptions are probably incorrect, in addition to which it has not been definitely proved that boiling with an alkaline solution of mercuric cyanide wholly destroys the optical activity of maltose and dextrose, while leaving that of dextrin unchanged. Nor has the action of the mercuric solution on the indefinite carbohydrates been ascertained with certainty, though they may be presumed to react like maltose, since "gallisin" is stated to reduce Knapp's solution. Haas also found that certain samples of starch glucose gave concordant results with Fehling's and Sachsse's solutions, while in other cases the reducing action of the latter reagent showed 10 per cent. more reducing matter (in terms of dextrose). Haas suggests (*Zeits. Anal. Chem.*, xxii. 219) that the difference was due to the presence of unfermentable carbohydrates, but offers no proof of the accuracy of this view, and makes no mention of maltose, which also reduces Sachsse's solution.

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[1] If the directions in the text were adhered to, and a sample showed an angular rotation of 3°·2 with a tube 4 decimetres in length, then the calculation would be :—

$$\frac{3{\cdot}2 \times 1000 \times 50}{198 \times 40 \times 1} = 20{\cdot}20 \text{ per cent. of dextrin.}$$

704. Wiley's process was employed by the Committee of the American Academy of Sciences appointed to investigate the nature of commercial starch glucose.[1] Their Report to the United States Commissioner of Internal Revenue is a valuable contribution to the literature of the subject. The following is an epitome of the results quoted in the Committee's Report:—

	Solid Forms. Per cent.	Liquid Forms. Per cent.
Dextrose, ...	72·0 to 73·4	34·3 to 42·8
Maltose, ...	0·0 to 3·6	0·0 to 19·3
Dextrin, ...	4·2 to 9·1	29·8 to 45·3
Ash, ...	0·33 to 0·75	0·32 to 1·06
Water, ...	14·0 to 17·6	14·2 to 22·6

705. Probably a more certain method of estimating the dextrin in commercial glucose would be to employ the following method recommended by C. Graham:—Dissolve 5 grammes of the sample in a small quantity of hot water, and add the solution drop by drop to 1 litre of nearly absolute alcohol. Dextrin is precipitated, and on standing becomes attached to the sides of the beaker, while maltose, gallisin, and dextrose are soluble in the large quantity of alcohol employed. If the solution be then decanted from the precipitate the *dextrin* in the latter can be ascertained by drying and weighing, or by dissolving it in a definite quantity of water and observing the solution-density and rotation. The alcohol is distilled off from the solution of the sugars, and the residual liquid divided into aliquot portions, in one of which the *gallisin* may be determined after fermentation with yeast, while others are employed for the observation of the specific rotation and reducing power, which data give the means of calculating the proportions of *maltose* and *dextrose* in the sample. In the absence of gallisin these may also be deduced from the increase in the reducing power caused by heating with dilute acid for several hours (par. 507).

The method indicated in the last paragraph is probably the best existing for the complete analysis of starch glucose, but it must be admitted that no reasonably simple process has hitherto been suggested which will enable the constituents of all kinds of commercial glucose to be ascertained with a fair approximation to accuracy.[1]

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[1] In a copy of the report sent to the writer by one of the members of the committee, the following note is made respecting a sample found by Wiley's method to contain 41·5 per cent. of dextrose, 0·6 of maltose, and 38·8 of dextrin. "This sample when fermented gave results which lead us to the belief that it contains a large amount of maltose, and very little, if any, dextrose. From this and some other facts noticed in the course of the work, we conclude that the method of Wiley is not applicable to products containing any considerable percentage of maltose." Nevertheless Wiley's process is a distinct advance toward the solution of a very difficult problem.

706. When cane or invert sugar is also present, as is frequently the case in confectioners' glucose syrup and factitious honey, the problem is still more complete, though an approach to its solution is given in par. 553. The estimation of starch glucose when employed as an adulterant of commercial cane sugar is described in par. 583 *et seq.*

707. The *water* in commercial glucose may be determined by one of the methods described in par. 568 *et seq.*, but a high temperature must be carefully avoided. H. W. Wiley has communicated to the author the following method of determining the water in commercial glucose. The process is also applicable to molasses, honey, &c.:—Two grammes of the sample is treated in a flat platinum dish with a few centimetres of dilute alcohol (40 per cent.) until completely dissolved, when a weighed quantity (10 to 15 grammes) of dry sand (previously washed and ignited) is added, and thoroughly mixed with the liquid by means of a weighed glass rod. The dish is then heated over boiling water for one hour, when the contents are moistened with about 5 c.c. of absolute alcohol and further heated to 100° for ten minutes. The dish is then heated to 110° in an air-bath for fifty minutes, and weighed.

708. The *ash* of commercial glucose should not exceed 1 per cent. of the weight of the sample, and should be almost wholly free from iron, which is objectionable in brewing materials. It usually consists chiefly of calcium sulphate,[2] but this is not invariably the case. Sometimes the sulphate of calcium is removed by treating the concentrated solution of the glucose with barium oxalate, in accordance with a proposal of E. Luck.

709. The *nitrogenous matter* of glucose can be determined, if desired, by ignition with soda-lime. The amount of nitrogen found, multiplied by 6·33, gives the albuminoid matter. Fair comparative results may be obtained by Wanklyn's "albuminoid ammonia" process (see par. 218). Mere traces of nitrogenous matter should be present in good glucose, though it is

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[1] For an advance in this direction see footnote on page 311.

[2] J. S. C. Wells made, on behalf of the United States Committee (par. 704), a number of analyses of the ash of samples of commercial starch glucoses (Report, page 24). The composition varied very greatly, and the results showed clearly that calcium sulphate was by no means the nearly constant constituent of glucose-ash which it is commonly assumed to be. In not a few cases the proportion of chlorides exceeded that of the sulphates. Careful search was made for metallic impurities, but with wholly negative results.

true that some favourite commercial brands contain a notable proportion of albuminoids.

710. *Free Acid* ought to be wholly absent from commercial glucose, though many specimens possess normally a slightly acid reaction, which is probably due to acid phosphates.

711. **Honey.**

French—Meil. *German*—Honig.

Ordinary honey is a saccharine substance collected and stored by a particular species of bee (*Apis mellifica*), but its production is common to various species of bees, besides other hymenopterous insects, such as wasps and certain species of ants.[1]

712. The specific gravity of virgin honey ranges from 1425 to 1429, and that of honey from old bees from 1415 to 1422. According to Buchner, the density sometimes reaches 1440.

713. When honey is examined under the microscope, crystals of dextrose, scales from butterflies' wings, spores of fungi, and different kinds of pollen may be observed. The last bodies, if sufficiently identified, may lead to a knowledge of the country whence the honey was derived.

714. Chemically, honey is essentially a concentrated aqueous solution of certain sugars, dextrose and lævulose being the most important constituents. Occasionally a small percentage of sucrose appears to be normally present, especially in the new honey from bees fed on cane sugar,[2] but after a time this constituent undergoes inversion by the trace of acid or some ferment present in the honey. According to James Bell, honey contains from 5 to 10 per cent. of a substance which undergoes conversion to glucose only by prolonged treatment with acid (maltose, gallisin ?). Soubeiran and Dubrunfaut also state that honey contains certain undefined sugars, and the same conclusion is deducible from the analytical results of other observers.

715. Besides the true sugars, honey contains a sensible quantity of the saccharoid mannite, $C_6H_{14}O_6$ (see Table on page 189),

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[1] The Mexican honey-ant (*Myrmecocystus Mexicanus*), secretes a syrup of nearly pure invert sugar, but slightly acid, apparently from the presence of formic acid.

In a substance allied to honey called *tazma*, found in Ethiopia, and said to be the product of an insect like a large mosquito, A. Villiers found 32 per cent. of glucoses (the dextrose being somewhat in excess), *no* sucrose, 27·9 per cent. of a kind of dextrin, 3·0 of mannite, 2·5 of mineral matter, a non-nitrogenous bitter principle, and 9·1 of unidentified substances (*Compt. rend.*, lxxxviii. 292).

[2] On the other hand, the nectar of plants contains a considerable quantity of an invertible sugar, which is probably sucrose (*Chem. News*, xxxviii. 93).

which may be isolated by fermenting a solution of the honey with excess of yeast, filtering, evaporating the filtrate to a low bulk, adding excess of boiling alcohol, evaporating the filtered liquid to dryness, extracting the residue with boiling alcohol, concentrating the resultant solution, and precipitating the mannite therefrom by addition of ether.

716. The other constituents of honey are water, small quantities of wax, pollen, mineral matter, traces of flavouring and bitter substances, organic acids, &c. Formic acid appears usually to be present in honey.

717. Several observers have published figures showing the composition of honey, the most complete analyses being those of J. Campbell Brown (*Analyst*, iii. 269). E. Sieben (*Zeits. Anal. Chem.*, xxiv. 135), and O. Hehner (*Analyst*, ix. 64), have determined certain of the constituents in a large number of samples of honey, and J. Bell in a few (*Foods*, part i. p. 116). A. H. Hassall has also published analyses of four samples of honey. The following is an epitome of the results of these chemists :—

	J. C. Brown.	E. Sieben.	O. Hehner.	J. Bell.	A. H. Hassall.
Dextrose,	31·77 to 42·02	22·23 to 44·71	...	...	...
Lævulose,	33·56 to 40·43	32·15 to 46·89	...	...	...
Total Glucoses,	68·40[1] to 79·72	67·92 to 79·57	61·42 to 75·34	66·57 to 74·04	79·48 to 82·50
Sucrose,	...	none to 8·22	...	...	none to 5·29
Wax, Pollen, and Insoluble matters,	trace to 2·10	...	...	...	traces
Ash,	0·07 to 0·26	...	...	0·13 to 0·49	0·02 to 0·30
Water expelled at 100° C.	15·50 to 19·80	16·28 to 24·95	12·43 to 23·26	17·10 to 23·32	13·63 to 19·56
Undetermined matters (by difference),	4·95 to 11·00	1·29 to 8·82	8·48 to 19·17	7·67 to 10·79	

The undetermined matters of Bell's analyses included the unidentified sugar previously mentioned, while Campbell Brown collected a considerable quantity of water, which he found to be driven off above 100° C.

718. Although the figures representing the other constituents show a considerable range of variation, the great majority of samples of honey are of a remarkably constant character, the glucoses ranging from 70 to 80 per cent., the water from 17 to 20, and the ash from 0·10 to 0·25. In normal honey, the dextrose and lævulose are present in approximately equal proportions, but if the honey has crystallised in the comb the runnings therefrom

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[1] In this analysis there was also found 2·2 per cent. of cane sugar, but Dr Brown considers that the appearance of sucrose as a constituent is as probably due to error of experiment as to its actual presence in the specimen, which was one of Jamaica honey. Dr Brown's figures for dextrose and lævulose have been re-calculated with his consent.

will be deficient in dextrose, and hence will be strongly lævo-rotatory. It is held by experienced bee-keepers that all genuine honey will eventually crystallise, and hence that honey warranted to remain syrupy is probably adulterated.

719. Analysis of Commercial Honey.

Honey is frequently adulterated, the most common sophistication being the addition of glucose-syrup, a dextrino-saccharine liquid obtained by the action of dilute acid on starch (par. 688). A factitious honey is sometimes manufactured wholly from glucose syrup, with addition of minute quantities of formic acid, &c., to give the preparation a flavour of honey. Cane sugar and invert sugar have also been used as adulterants of honey, and molasses is said to have been occasionally added. The addition of mineral matters, such as clay or gypsum, at the present day is very improbable.

720. The proportion of *water* in honey may be determined as in molasses (par. 569), or by the method of Wiley, described in par. 717. A useful check on the result is obtained by calculating the solids from the density of a 20 per cent. solution of the sample, as described in par. 488.

721. The *ash* of genuine honey is usually very trifling in amount. If in excess of 0·3 per cent., it should be tested for *calcium sulphate*, the presence of which, in notable quantity, is an almost certain indication of adulteration by starch glucose or invert sugar. In fact, the presence of notable traces of sulphates is the only way in which an addition of invert sugar to honey can be inferred. Sulphates may also be detected by the direct addition of barium chloride to the aqueous solution of the sample. A high ash containing a notable proportion of *chlorides* points to a probable adulteration with molasses.

722. The *insoluble matter* of honey may be determined as in sugar. It usually consists of wax, pollen, &c., and should be carefully examined under the microscope. *Starch*, which is not a normal constituent of honey, will be readily recognised in the residue by its reaction with iodine, and, if present in quantity, points to an adulteration of the sample with *flour* or other farinaceous substance, the exact nature of which will be indicated by its microscopic appearance.

723. *Gelatin*, if present, will be left undissolved on treating the sample with spirit, and will be recognised by its odour on ignition, and the reaction of its aqueous solution with tannin.

724. *Dextrin*, which is not found in genuine honey, but is a constituent of commercial glucose syrup, may be detected by diluting the honey with an equal measure of water, and gradually

adding strong spirit, stirring constantly until a permanent turbidity is produced. In samples adulterated with *glucose syrup* a heavy gummy deposit will soon form, but with genuine honey only a slight milkiness is produced (see footnote on page 307).

725. Saccharine additions to honey can only be detected by a careful examination of the action of the sample on polarised light, and its behaviour with Fehling's and other reducible solutions. The following table shows the specific rotatory power and cupric oxide reducing power of mixtures of cane and invert sugar, containing 82 per cent. of the solid and 18 per cent. of water, and of average glucose syrup, as compared with genuine honey. The table also shows the changes produced in solutions of the above saccharine matters by the action of invertin (par. 563), by prolonged heating with dilute acid (par. 507), and by fermentation with yeast (par. 513) :—

	Cane Sugar 82%, Water 18%	Invert Sugar 82%, Water 18%.	Average Glucose Syrup.	Genuine Honey.
SPECIFIC ROTATORY POWER FOR SODIUM RAY.				
Original substance, . .	+54·5	−18·9 at 15°	+92 to 100	+2 to−3
After treatment with invertin, ...	−19·9 at 15°	−18·9 at 15°	little altered	little altered.
After prolonged heating with dilute acid, . . .	−19·9 at 15°	−18·9 at 15°	+45	little altered.
After fermentation with yeast, ...	inactive	inactive	very notably dextro-rotatory	0 to+4
CUPRIC OXIDE REDUCING POWER.				
Original substance, . .	0	82	53	61 to 82
After treatment with invertin, ...	86·3	82	little altered	little altered.
After prolonged heating with dilute acid, . . .	86·3	82	82	little altered.
After fermentation with yeast, ...	0	0	very notable	0 to 2

726. According to the table, there is a sensible difference between the rotation of *invert sugar* and genuine honey, but unfortunately this distinction does not always hold good, for if the honey has crystallised in the comb some of the dextrose is apt to remain there, and the honey drained therefrom will contain excess of lævulose, and be more strongly lævo-rotatory than is indicated by the figures in the table. Unless, therefore, the ash be excessive, or happen to contain calcium sulphate (par. 708), the positive recognition of added invert sugar is next to impossible.

727. Any considerable proportion of *cane sugar* in honey would be indicated by the strong dextro-rotation of the sample, changed

to left-handed rotation on treatment with invertin or dilute acid. The proportion of cane sugar can be estimated from the extent of the *change* in the rotatory and reducing power of the sample caused by treatment with invertin, or, in the absence of glucose syrup, by inversion with dilute hydrochloric acid, as in par. 477. As already stated, a small percentage of sucrose appears sometimes as a constituent of genuine honey.

728. *Glucose syrup* is still more dextro-rotatory than cane sugar to commence with, the optical activity falling to about one-half by prolonged treatment with acid, while the products left after fermentation are still notably dextro-rotatory. In the absence of added cane and invert sugar, an approximate estimation of the proportion of glucose syrup in honey may be made by reckoning 1 per cent. of the adulterant for every degree of dextro-rotatory power possessed by the original sample. Of course, it must not be forgotten that a dextro-rotation of a few degrees is observable in some samples of genuine honey.[1] The saccharine liquid secreted by fir-cones, etc., is said to be notably dextro-rotatory.

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[1] Sieben, in a recent valuable paper (*Analyst*, x. 34), gives the following methods of examining honey for starch glucose:—For the fermentation test, 25 grammes of the sample are dissolved in water, the solution diluted 200 c.c., and fermented for forty-eight hours at the temperature of the room with 12 grammes of German yeast free from starch. Alumina cream (page 201) is then added, the liquid diluted to 250 c.c. and filtered. 200 c.c. of the clear filtrate should then be evaporated to 50 c.c., and examined in the polarimeter. As already stated, pure honey gives a residue after fermentation which is optically inactive, or nearly so, while the residue from an adulterated sample is strongly dextro-rotatory. Sieben states that, operating as above described, a sample adulterated with 20 per cent. of starch sugar will show a rotation of +7°·2 when examined in a 2-decimetre tube with a Wild's polarimeter, while a sample containing 50 per cent. of starch sugar will rotate +22°·2 under the same conditions. After observing the optical activity, 25 c.c. of the (fermented and concentrated) solution employed for the experiment should be heated on the water-bath with 25 c.c. of water and 5 c.c. of concentrated hydrochloric acid. The liquid is then neutralised, made up to 100 c.c., and the sugar determined in 25 c.c. by Fehling's solution. The glucose thus found, when multiplied by 40, gives the dextrose corresponding to the unfermentable carbohydrates of the sample. Honey containing 10 per cent. of starch sugar shows 3·24 per cent. of dextrose from the unfermentable matters, while 20 per cent. gives 6·39, and 40 per cent. 8·85 of dextrose. Unfortunately, all these figures assume the presence of constant proportions of unfermentable carbohydrates in honey and starch sugar.

Another method of detecting starch sugar in honey, described by Sieben as being very delicate, is as follows:—14 grammes of honey are dissolved in about 450 c.c. of water, and any sucrose inverted by heating the solution with 20 c.c. of semi-normal hydrochloric acid. The liquid is then neutralised, and

729. Glucosides.

The name glucoside is applied to numerous bodies possessing the common property of yielding glucose, $C_6H_{12}O_6$, as one of the products of their treatment with water and a dilute acid. Thus salicin, when boiled with dilute sulphuric acid, yields dextrose and the alcohol-like body saligenol or saligenin.

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_5 + C_7H_7O.OH .$$

A similar decomposition of the glucosides often occurs by the agency of certain peculiar ferments occurring in the plant together with the glucoside. These ferments have a very limited power of producing such decompositions, their influence being exerted only on a few glucosides of closely-related composition.

The nature of the glucoses obtained from the glucosides has been identified with sucro-dextrose in a few instances (see par. 677), but in the majority of cases the exact nature of the resultant glucose is still uncertain.

730. Some of the glucosides are of interest from a pharmaceutical and toxicological point of view, but few of them, except gallotannic acid and the glucoside of mustard, commonly require to be assayed. Their analytical characters have in most cases been but very imperfectly studied. From the alkaloids they may, as a rule, be separated by acidulating the aqueous liquid with sul-

made up to 100 c.c. 100 c.c. of Fehling's solution are next titrated with the saccharine solution, of which 23 to 26 c.c. will be required; and then another quantity of 100 c.c. of Fehling's solution is boiled with a measure of the honey solution less by 0·5 c.c. than was previously found necessary for the reduction of the copper. By this means the sugars are oxidised without the non-reducing carbohydrates being affected. The liquid is filtered through asbestos, the filter washed slightly with hot water, and the filtrate neutralised with strong hydrochloric acid. One-tenth of its measure of fuming hydrochloric acid is then added, and the solution is heated on the water-bath for one hour, *nearly* neutralised with concentrated solution of soda, and made up to 200 c.c. After cooling, the liquid is passed through a dry filter, and 150 c.c. of the filtrate boiled with 120 c.c. of Fehling's solution and 20 c.c. of water. The dextrose corresponding to the non-reducing carbohydrates is calculated from the cuprous oxide precipitated. Sieben states that when treated in the above manner the metallic copper corresponding to the cuprous oxide precipitated by genuine honey does not exceed 0·002 gramme, while with 5 per cent. of starch sugar the copper precipitated weighs ·020; with 10 per cent., ·040; with 20, ·090; with 40, ·190; and with 60, ·330 gramme. These figures again assume the presence of a constant proportion of non-reducing carbohydrates in the starch sugar used as the adulterant.

The foregoing methods of examination would probably yield interesting and valuable results if employed for the analysis of unmixed starch glucose.

phuric acid, and agitating with a mixture of chloroform and ether, which extracts the glucosides without affecting the sulphates of the majority of the alkaloids. The alkaloids which cannot thus be separated are usually weak bases. Some facts respecting the behaviour of certain glucosides with immiscible solvents will be found on page 33, and more detailed information will be given in future sections of the work.

STARCH AND ITS ISOMERS.

731. In the vegetable kingdom, and to a minor extent in the animal kingdom, there exist a number of carbohydrates having in common a composition represented by the empirical formula $C_6H_{10}O_5$, but their physical and chemical characters point in many cases to a multiple of this formula as the true representation of the constitution of the molecule.

The carbohydrates of the starch-group are non-volatile bodies, and, with perhaps one or two exceptions, are amorphous. As a class they are insoluble in alcohol, though the greater number of them are dissolved by water, forming solutions which usually exert a marked rotatory action on a ray of polarised light. They are neutral in reaction, and form but few definite compounds or metallic derivatives. The carbohydrates of the starch group are very numerous, and apparently capable of isomeric modification. Owing to their physical characters, and feebly-marked chemical affinities, it is often extremely difficult to obtain them in a state of purity.

732. None of the members of the group reduce Fehling's solution when boiled with it. By treatment with acids they yield sugars among other products, and then reduce the cupric solution.

733. The members of the group are many of them of little practical interest, and their analytical reactions have been very incompletely studied. The following table serves to show the comparative characters of the more important members of the group, and cellulose, starch, and dextrin are described more fully in subsequent sections. In par. 844 will be found tables for the general proximate analysis of plant-products; and under the head of "Gums" a short description of pectinous ma

Name.	Empirical Formula.	Chief Sources and Modes of Formation.	Specific Rotatory Power.	Solubility in Water.	Products obtained by boiling with dilute Acid.	Reaction with Iodine Solution.	Other Characters.
Cellulose.	$C_6H_{10}O_5$.	Cotton-wool; filter-paper; linen rags.	...	Not soluble.	Not changed.	No change; blue in presence of zinc chloride.	Soluble in Schweitzer's reagent, forming lævo-rotatory solution. With strong sulphuric acid, followed by dilution, gives dextrose, &c.
Starch.	$C_6H_{10}O_5$.	Amylaceous seeds, roots, &c.	$S_D=+200$ $S_j=+222$	Insoluble, cold; gelatinised and dissolved on boiling.	Maltose and dextrin; ultimately dextrose.	Violet-blue.	White powder of characteristic appearance under microscope. Insoluble in Schweitzer's solution. Precipitated by tannin and ammoniacal lead acetate.
Glycogen.	$6C_6H_{10}O_5+H_2O$.	Liver of man and herbivorous animals; oysters.	$S_D=+203$ to $+223$	Slowly soluble; solution opalescent, cleared by acetic acid.	Dextrose.	Wine-red.	White amorphous body, readily soluble in alkaline liquids.
Inulin.	$C_6H_{10}O_5$.	Elecampane; dahlia; dandelion; chicory.	Lævo-rotatory	Cold, slightly soluble; hot, readily soluble.	Lævulose.	No change.	White, hygroscopic powder, or sphæro-crystals, containing $6C_6H_{10}O_5,H_2O$. Insoluble in absolute alcohol, sparingly in dilute. Reduces ammonio-nitrate of silver.
Dextrin.	$C_6H_{10}O_5$.	Action of acids or diastase on starch.	$S_D=+200$ $S_j=+222$	Readily soluble.	Dextrose.	Erythro-dextrin, reddish-brown; achro-dextrin, colourless.	White, very deliquescent. Apparently two varieties, differing in their reaction with iodine. Insoluble in alcohol.
Lævulin.	$C_6H_{10}O_5$.	Dahlia; Jerusalem artichoke.	Inactive.	Soluble.	Lævulose and dextrose.	...	Amorphous, insipid, deliquescent. Ferments slowly with yeast.
α-Amylan.	$C_6H_{10}O_5$.	Barley, &c.	$S_j=-24$	Cold, nearly insoluble; hot, gelatinises and dissolves sparingly.	Dextrose.	No change.	Amorphous, white substance.
β-Amylan.	$C_6H_{10}O_5$.	Wheat, rye, &c.	$S_j=-144$ to -148	Soluble in cold water, forming very viscous solution.	A dextro-glucose.	No change.	Amorphous, white substance. Fresh solution exhibits bi-rotation.
Lichenin.	$C_6H_{10}O_5$.	Iceland moss.	—	Soluble in hot water; gelatinises on cooling.		No change.	Insoluble in alcohol and in Schweitzer's solution.
Gums.	...	...	Lævo-rotatory.	Soluble in, or swollen by, cold water.	Glucoses.	No change.	Amorphous. Solutions highly colloid. Insoluble in alcohol. Yield mucic acid by treatment with nitric acid.

734. **CELLULOSE.** $C_6H_{10}O_5$.

Cellulose constitutes the essential part of the solid frame-work or cellular tissue of plants, and hence is an especially characteristic product of the vegetable kingdom. The outer coating of Ascidian animals is, however, apparently identical with cellulose.

Cellulose occurs nearly pure in cotton, linen, and the pith of certain plants. Swedish filter-paper, linen rags, and cotton-wool are still purer forms of cellulose.

Cellulose is closely related to starch, and is most probably directly formed from it; but it is more stable than starch, and is not readily rendered soluble.

735. Cellulose is a white, tasteless, odourless, non-volatile body of about 1·45 specific gravity. It is insoluble in water and all ordinary menstrua, but dissolves, as first observed by Schweitzer, in a strong solution of cupric oxide in ammonia.

736. SCHWEITZER'S REAGENT, which may be regarded as a solution of cupr-ammonium hydroxide, is prepared by leaving copper turnings partially immersed in ammonia, with access of air. Or cupric hydrate may be precipitated from a cold solution of cupric sulphate by adding excess of caustic soda, and the well-washed precipitate dissolved to saturation in ammonia. On treatment with the resultant solution, cellulose becomes gelatinous, and on agitation gradually dissolves, forming a viscid solution which may be filtered after dilution with water.[1] On neutralising the filtrate with hydrochloric acid the cellulose is separated in a flocculent state resembling hydrated alumina, which when dried forms a brittle, greyish, horn-like mass. Carbonic acid also precipitates the solution, as do sugar, salt, and even copious dilution with water.

The solution of cellulose in Schweitzer's reagent is decomposed by dialysis. It is *lævo*-rotatory, a 1 per cent. solution showing a specific rotation of $-20°$ for the light transmitted, which bears to the sodium ray the ratio 1 : 1·85. The optical activity is not strictly proportional to the cellulose dissolved, increasing somewhat more slowly than the concentration of the solution. Cellulose from different sources exhibits the same optical activity.

737. According to Fremy, three varieties of cellulose exist, all of which are soluble without coloration in cold sulphuric acid of 1·78 specific gravity, to form a solution which, after dilution with water and boiling, is found to contain glucose; they are distinguished by their behaviour with the cupric solution; thus :—

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[1] The action of ammoniacal solutions of cupric and zinc oxides on cellulose has been applied on a large scale by C. R. Alder Wright to the manufacture of the "Willesden" products (*Jour. Soc. Chem. Ind.*, iii. 121).

a. Cellulose; constituting the greater part of cotton and the utricular tissue of certain fruits, as the apple, is dissolved immediately by the cupric reagent.

b. Paracellulose; forming the epidermis of leaves and the utricular tissue of certain roots, is not soluble in the cupric solution till after boiling with very dilute hydrochloric acid.

c. Metacellulose, or *fungin*; found chiefly in agarics and lichens, is not dissolved by the cupric reagent even after treatment with acid, but is easily soluble in nitric acid and in hypochlorites, and is distinguished from the *a* and *b* varieties of cellulose by its solubility in cold sulphuric acid diluted with 4 or 5 equivalents of water.

738. Cellulose is not altered by cold dilute alkaline solutions, but in concentrated caustic potash or soda it swells up and gradually dissolves, being apparently converted into dextrin and ultimately into sugars. Cellulose absorbs an appreciable amount of barium hydrate when immersed in dilute baryta water.

By heating to a high temperature with caustic potash, cellulose yields methylic alcohol and potassium oxalate.

When heated with a solution of a hypochlorite containing free alkali, or with soda and a ferricyanide, cellulose forms oxidation-products which are soluble in the alkaline liquid.

739. Cellulose does not undergo the ordinary alcoholic fermentation with yeast, but in presence of a little albuminoid matter it is converted by the ferment of the pancreas into acetic and isobutyric acids, methane and carbon dioxide being simultaneously evolved (Tappeiner, *Ber.* xvi,. 1734).

740. If cotton-wool or filter-paper be heated at 180° C. for several hours with about six or eight parts of acetic anhydride, it is entirely dissolved and converted into a triacetate, $C_6H_7(C_2H_3O)_3O_5$, which may be separated by pouring the syrup into water; it is a white powder, optically inactive, soluble in strong acetic or sulphuric acid, and very readily converted into cellulose and potassium acetate by boiling with dilute caustic potash. Other acetyl-derivatives of cellulose have been obtained.

741. HYDROCELLULOSE, $C_{12}H_{22}O_{11}$, is the product of the action of mineral acids, (*e.g.*, sulphuric acid of 1·42 sp. gr., or fuming hydrochloric acid) and many other reagents on cellulose. It always retains the form of the cellulose from which it is derived, but differs therefrom in being extremely friable, more readily affected by reagents, and in the readiness with which it combines with colouring matters.

Cellulose undergoes gradual change by prolonged boiling with dilute acids, being converted into hydrocellulose, and is even affected by boiling water alone, especially if heated under pressure.

742. Cold concentrated sulphuric acid dissolves cellulose, converting it first into a body (? hydrocellulose) which gives a blue colour with iodine, and swells up in water without dissolving; a dextrinoid substance is next produced, and if the liquid be then largely diluted and boiled, sugars are formed which reduce Fehling's solution. If cellulose be heated with concentrated sulphuric acid, charring at once occurs.

By treating cellulose with cold sulphuric acid previously diluted with half its measure of water, it is converted into a substance called amyloid, which, after washing with cold water, is extraordinarily tough. This fact is utilised for the production of "parchment paper." Chloride of zinc may be substituted for the sulphuric acid.

743. Cellulose is not coloured by iodine solution alone, or at most only assumes a yellow or brownish colour, but in presence of hydriodic acid, potassium or zinc iodide, zinc chloride, sulphuric or phosphoric acid, it is coloured blue by iodine. Concentrated sulphuric acid and zinc chloride especially favour the production of the blue colour, doubtless owing to the formation of amyloid.[1] If cellulose be first treated with one of the above reagents, and then freed from it by washing, no blue colour is produced on adding solution of iodine.

744. By treatment with cold nitric acid of 1·42 specific gravity, cellulose is remarkably toughened, without losing its fibrous structure or becoming nitrated. With stronger acid, cellulose is converted into nitro-substitution products which are described in par. 773 *et seq.*

By boiling with moderately concentrated nitric acid, cellulose is converted into oxidation-products, some of which have a close analogy to the original substance, but differ from it in certain remarkable respects.

745. Oxycellulose appears tó vary somewhat in composition according to the mode of preparation, but an apparently definite substance of the formula $C_{18}H_{26}O_{16}$ was obtained by Cross and Bevan (*Jour. Soc. Chem. Ind.*, iii. 206) from several different sources. The cellulose was boiled with nitric acid containing 50 per cent. of HNO_3, whereby it was largely oxidised to oxalic acid, but yielded 30 per cent. of oxycellulose in the form of a fine white powder, readily soluble in dilute alkalies and reprecipitable from the solution in a pectous form on addition of acids, salts, or alcohol. Oxycellulose dissolves in concentrated sulphuric acid with pink coloration, and yields a gummy dextro-rotatory substance resembling

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[1] Schulze's reagent, by which cellulose is coloured blue, may be prepared by adding 6 grammes of iodine and the same weight of potassium iodide to 100 c.c. of a solution of zinc chloride of 1·8 specific gravity.

ordinary dextrin. By the action of concentrated nitric acid mixed with sulphuric acid, oxycellulose yields a nitro-compound of the formula $C_{18}H_{23}(NO_2)_3O_{16}$.

746. The action of hypochlorites on cellulose, which has an important practical bearing on the theory and practice of bleaching cotton and linen goods, has been studied by M. G. Witz. By the extreme action of the reagent, the cellulose is converted into a white friable powder, which is a variety of oxycellulose. If the action of the bleaching solution be duly controlled the cellulose is unchanged in appearance, but is now found to be remarkably modified in its relation to colouring matters. Thus all the basic coal-tar dyes (and notably methylene blue) dye oxycellulose without requiring a mordant, while the dyes of acid character do not exhibit the slighest affinity for it. The absorptive power of oxycellulose for vanadium is so great as to withdraw it from a solution containing only one-billionth of the metal, and the combination can be demonstrated by printing the tissue with aniline-black mixture.

The oxidation of cellulose by hypochlorites seems to depend on the presence of free acid,[1] even the atmospheric carbonic acid having a notable influence. When once converted into oxycellulose, no reducing agent (*e.g.*, thiosulphate) will restore the fibre to its original condition. By immersing dyed oxycellulose-tissue in a bleaching liquid, the dye can be made to disappear, and the fibre can be re-dyed of any colour by immersion in the solution of a suitable colouring matter.

When an oxycellulose-tissue is boiled with Fehling's solution cuprous oxide is formed, and becomes deposited in firm union with the fibre, dyeing it an orange colour.

747. DETERMINATION OF CELLULOSE.

In consequence of its occurrence in association with bodies of a closely allied nature, the accurate determination of cellulose is often a tedious operation, and some, at least, of the processes prescribed for the purpose yield arbitrary rather than accurate results.

748. From *starch*, cellulose is best separated by boiling the substance with water containing 1 per cent. by measure of sulphuric acid. The liquid is filtered when a drop taken out gives no coloration with iodine solution. In cases where the use of acid is objected to, the substance should be boiled with water, and the unfiltered liquid mixed with an equal measure of cold infusion of malt. The starch will be wholly dissolved by keeping the liquid at a temperature of 60° C. for a short time.

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[1] If paper be written on with a solution of potassium chlorate acidulated with hydrochloric acid, oxycellulose is formed, and on immersing the paper in a solution of a basic coal-tar dye the writing will appear in colour.

749. The separation of cellulose from *sugar*, *dextrin*, and other substances soluble in water presents no difficulty. *Albuminoids* may be separated by treatment with warm water containing 1 per cent. of caustic alkali. They may be determined by igniting the substance with soda-lime.

750. For the determination of cellulose in wood, vegetable fibres, and substances to be used for the manufacture of paper, Müller recommends the following process :—5 grammes weight of the finely-divided substance is boiled four or five times with water, using 100 c.c. each time. The residue is dried at 100° C., weighed, and exhausted with a mixture of equal measures of benzene and strong alcohol, to remove fat, wax, resin, &c. The residue is again dried, and boiled several times with water to every 100 c.c. of which 1 c.c. of strong ammonia has been added. This treatment removes colouring matter and pectous substances. The residue is further bruised in a mortar, if necessary, and is then treated in a closed bottle with 250 c.c. of water, and 20 c.c. of bromine water containing 4 c.c. of bromine to the litre. In the case of the purer bark-fibres, such as flax and hemp, the yellow colour of the liquid only slowly disappears, but with straw and woods decolorisation occurs in a few minutes. When this takes place, more bromine water is added, and this is repeated till the yellow colour remains and bromine can be detected in the liquid after twelve hours. The liquid is then filtered, and the residue washed with water and heated to boiling with a litre of water containing 5 c.c. of strong ammonia. The liquid and tissue are usually coloured brown by this treatment. The undissolved matter is filtered off, washed, and again treated with bromine water. When the action seems complete, the residue is again heated with ammoniacal water. This second treatment is sufficient with the purer fibres, but the operation must be repeated as often as the residue imparts a brownish tint to the alkaline liquid. The cellulose is thus obtained as a pure white body. It is washed with water, and then with boiling alcohol, after which treatment it may be dried at 100° C. and weighed.

751. Bevan and Cross (*Chem. News*, xlii. 77), substitute a treatment with chlorine gas for the repeated digestion with dilute bromine water prescribed in the foregoing process. A single repetition of the treatment is then always sufficient, and the results obtained are concordant with those given by the bromine process. Bevan and Cross also find that by boiling the chlorinated fibre for a few minutes in a 5 per cent. solution of sodium sulphite, and then in a 1 per cent. solution of caustic potash, pure cellulose is at once obtained,—the results by this method being 5 per cent. higher than those yielded by Müller's process.

752. Analysis of Woody Tissues.

Cellulose is associated in woody tissues with ligneous, cuticular, and intercellular bodies. These have the following analytical characters :—

753. LIGNIN, VASCULOSE, or ligneous matter cements the fibres and cells together, and constitutes the hard part of woody tissue. The harder the wood the larger the proportion of lignin contained in it.

Lignin contains more carbon than cellulose, having the composition $C_{18}H_{20}O_8$, according to Fremy, and $C_{19}H_{18}O_8$ according to Schuppe (*Pharm. Jour.*, [3] xiv. 52), while other observers appear to have analysed more hydrated bodies. It is doubtful whether lignin is a definite compound.[1] It is a light yellow substance, which retains the structure of the tissue from which it has been prepared. It has a density of 1·5, and is insoluble in all neutral liquids, as also in cold sulphuric acid of 1·78 specific gravity, and in ammonio-cupric oxide solution. It is also undissolved by alkalies under ordinary conditions, but dissolves when heated with them under pressure at 130° C., with formation of a brown liquid, from which acids precipitate black flocks of a complex composition. By fusion with caustic potash lignin is immediately converted into ulmic acid, while cellulose, when similarly treated, yields acetic and oxalic acids. The acetic acid produced in the distillation of wood appears to be derived chiefly, and the methyl alcohol wholly, from the vasculose. Treatment with dilute nitric acid, chromic acid, permanganate, chlorine, or bromine, converts lignin into bodies soluble in dilute alkalies, and partly even in water and alcohol. The products are resinous acids, of which those first formed are nearly insoluble in alcohol, while the final products are soluble both in alcohol and in ether. Lignin undergoes a similar change by atmospheric oxidation, as observed in the decaying of wood.

754. The presence of ligneous matter in vegetable tissues, such as hemp, flax, or paper, may be detected by exposing the wet substance to the action of chlorine or bromine, and then immersing it in a

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[1] (See abstract of researches by M. Singer in *Jour. Chem. Soc.*, xlii. 1122). According to Erdmann, pine wood consists of glucolignose, $C_{30}H_{46}O_{21}$, which can be obtained pure by treating the finely-rasped wood successively with very dilute acetic acid, hot water, alcohol, and ether. Traces of cellulose are next removed by Schweitzer's reagent when pure glucolignose remains. This is a glucoside, which on boiling with dilute hydrochloric acid yields glucose and lignin. Bente has confirmed Erdmann's formula for glucolignose, which he also prepared from poplar wood, but he differs from Erdmann as to the proportion of glucose formed by the action of acid.

neutral solution of sodium sulphite, when a fine purple coloration will be produced.

Ligneous matter is generally stated to be capable of detection by moistening the substance with an aqueous solution of aniline sulphate, which produces an intense yellow coloration. More accurate observations, however, have shown that the reaction is really dependent on the presence of products of the oxidation of cellulose, and does not occur if the tissue has been previously boiled in a solution of sodium sulphite.

A more certain and delicate test for vasculose consists in moistening the tissue with a solution ($\frac{1}{2}$ per cent.) of phloroglucinol, and then adding hydrochloric acid, when an intense red-violet coloration will be produced if lignin be present. The phloroglucinol may be replaced by resorcinol, orcinol, pyrocatechol, and similar bodies, but they are less convenient and reliable.

According to Reichl, if woody fibre be boiled with a solution of stannic chloride mixed with a few drops of pyrogallol, a fine purple coloration is produced.

755. Cutose, or cuticular substance, constitutes the greater part of cork, and the fine transparent membrane covering the exposed parts of vegetables. It contains a high percentage of carbon ($C=68·29$; $H=8·95$), and yields suberic acid, $C_8H_{14}O_4$, on oxidation with nitric acid of 1·20 specific gravity. Cutose is insoluble in cold sulphuric acid of 1·78 specific gravity, and in the ammonio-cupric solution which dissolves cellulose. On the other hand, it dissolves slowly in a hot dilute solution of sodium hydrate or carbonate, forming a solution from which acids precipitate a yellowish, flocculent substance, fusible below 100°, soluble in alcohol and ether, and having the same composition as cutose. If the alkaline solution be saturated with common salt, a cutose-soap rises to the surface. From the researches of Urbain, cutose appears to be composed of stearocutic acid, $C_{28}H_{48}O_4$, with five equivalents of oleocutic acid, $C_{14}H_{20}O_4$.

756. Pectose occurs in the utricular tissues of fruits and roots. It is insoluble in water, but is converted into soluble pectin by boiling with dilute hydrochloric acid. The solution obtained is precipitated by alcohol.

757. Calcium Pectate forms part of the membrane which binds the cells together. On treatment with cold dilute hydrochloric acid, pectic acid is liberated, and this may be dissolved in dilute alkali, and reprecipitated by an acid.

758. The following table gives a general outline of the method of analysing the *insoluble* portion of woody tissue. The sample

should be in the form of sawdust or shavings, or otherwise finely divided:—

All soluble matter having been previously removed by treatment with water, the sample is dried at 100°, and exhausted (preferably in a Soxhlet's tube, par 82.), with ether, and then with alcohol.					
Solution may contain *resins*, *colouring matters*, &c., determined by weighing the residue left on evaporation.	**Residue.**—Digest with cold, very dilute hydrochloric acid. Wash, and treat the residue with a cold dilute solution of caustic soda.				
	Solution contains alkaline *pectate*, from which insoluble *pectic acid* may be precipitated by adding HCl.	**Residue.**—Boil with dilute hydrochloric acid.			
		Solution.—Precipitate of *pectin* on addition of alcohol.	**Residue.**—Treat with cold sulphuric acid of 1·78 specific gravity.		
			Solution contains products formed from the *cellulose*.	**Residue.**—Boil with dilute caustic soda solution.	
				Solution contains *cutose*.	**Residue** consists of *lignin*, soluble in alkali after treatment with dilute nitric acid.

759. An alternative method, which is recommended by Urbain for the analysis of wood, consists in exhausting 20 grammes of the sample with ether and alcohol, then by distilled water, and by water made slightly alkaline by potash to remove soluble substances and *pectic compounds*, and finally with very dilute hydrochloric acid, which dissolves the lime and other *mineral matters*. The purified wood is weighed and treated with Schweitzer's cupric solution, and the residue washed, dried, and weighed. The loss is *cellulose*. The residue is boiled with weak hydrochloric acid for a few minutes, and again repeatedly treated with the ammonio-cupric reagent to dissolve the *paracellulose*. The residue, after washing, consists of pure *vasculose*. The results may be confirmed by dissolving out the two varieties of cellulose together by sulphuric acid, and weighing the residual vasculose, or by removing the vasculose with cold dilute nitric acid, boiling with ammonia, and weighing the residual cellulose. Some varieties of wood, *e.g.*, boxwood, yield no true cellulose when analysed, the insoluble portion being composed entirely of paracellulose and vasculose.

760. Pith parenchyma contains the same constituents as wood, and may be analysed in a similar manner. Purified elder-pith contains 37 per cent. of cellulose, 38 of paracellulose, and 25 of vasculose.

The following figures show the percentage results obtained by Urbain on applying the foregoing method to the analysis of typical woods, &c.:—

	Water and Extractives.	Cellulose and Paracellulose.	Vasculose.
Poplar,	18	64	18
Oak,	19	53	28
Box,	38	28	34
Ebony,	45	20	35
Iron-wood,	33	27	40
Walnut shell,	31	25	44
Cocoa-nut shell,	17	25	58

761. Cork contains cutose in addition to the constituents of wood. After purification, the *cutose* may be estimated from the loss of weight undergone on boiling the sample with dilute caustic alkali. Urbain found in common cork:—water, 2; matters soluble in ether or alcohol, 9; matters dissolved by water, dilute ammonia, and dilute hydrochloric acid, 5; cutose, 43; vasculose, 29; cellulose and paracellulose, 12 per cent.

762. Root-tissue contains paracellulose, vasculose, and often pectose in addition. The last may be dissolved by boiling the purified tissue with weak hydrochloric acid, and the vasculose and paracellulose separated as before.

763. The parenchyma of leaves is chiefly cellulose, and may be separated from the epidermis, fibres, and vessels by maceration with water or by treatment with Schweitzer's cupric reagent. The epidermis is composed of two closely-united membranes, the outer consisting of cutose and the inner of paracellulose. The latter can be dissolved away from the former by treatment with Schweitzer's reagent after boiling with dilute hydrochloric acid, or by treatment with cold sulphuric acid diluted with 3½ equivalents of water. The petals of flowers contain the same insoluble constituents as leaves.

764. The fibre of jute, for the characteristic constituent of which the name of *bastose* has been suggested, presents many peculiarities. It appears to consist of about 70 per cent. of cellulose, with a considerable quantity of a body allied to lignose. Jute fibre has formed the subject of a series of interesting papers by Bevan and Cross (*Chem. News*, xlii. 79, 91; xliv. 64; xlvii. 111; *Jour. Soc. Chem. Ind.*, i. 129; iii. 206, 291; *Jour. Chem. Soc.*, xlii. 18).

765. Recognition of Vegetable Fibres.

As vegetable fibres, when thoroughly bleached, all consist of nearly pure cellulose, chemical tests are not available for distinguishing one kind from another; but, owing to the impossibility of wholly removing the incrusting matter on the large scale, it is possible to distinguish between certain fibres, such as cotton and linen.

By far the best and most reliable means of differentiating vegetable fibres is to examine their structure with a microscopic power of 120 to 150 diameters.

766. The filaments of *cotton* appear under the microscope as transparent tubes about ·04 millimetre in diameter, flattened and twisted round their axis, and tapering off to a closed point at each end. A section of the filament resembles somewhat a figure of 8, the tube, originally cylindrical, having collapsed most in the middle, forming semi-tubes on each side, which give to the fibre when viewed in certain lights the appearance of a flat ribbon with a hem or border at each edge. The uniform transparency of the filament is impaired by small irregular figures, in all probability wrinkles or creases arising from the dessication of the tube. The twisted and corkscrew form of the dried filament of cotton distinguishes it from all other vegetable fibres, and is characteristic of the fully ripe and mature pod, M. Bauer having ascertained that the fibres of the unripe seed are simply untwisted cylindrical tubes, which never twist afterwards if separated from the plant; but when the seeds ripen, even before the capsule bursts, the cylindrical tubes collapse in the middle, and assume the form already described. This form and character the fibres always retain, undergoing no change through the various operations of spinning, weaving, bleaching, printing, and dyeing, nor in all the subsequent domestic processes of washing, &c., and even the reduction of the rags to pulp for the manufacture of paper effects no change in the structure of the fibres.

767. *Linen*, or *flax fibre*, appears under the microscope as hollow cylindrical tubes, open at both ends, and having a diameter of about ·02 of a millimetre. The fibres are smooth, the inner tube very narrow, and joints or septa appear at intervals, but they are not furnished with hairy appendages as is the case with hemp. The jointed structure of flax is only perceptible under a very excellent instrument, and with judicious management of the light.

When flax fibre (linen) is immersed in a boiling solution of equal parts of caustic potash and water for about a minute, and then removed and pressed between folds of filter paper, it assumes a dark yellow colour, whilst cotton when similarly treated either remains white or becomes a very bright yellow. The same solution of potash employed cold colours raw flax orange-yellow, whilst raw cotton becomes grey.

When flax or a tissue made from it is immersed in oil, and then strongly pressed to remove the excess of the liquid, it remains transparent, while cotton similarly treated becomes opaque.

768. *Phormium tenax*, or New Zealand flax, may be distinguished from ordinary flax or hemp by the red colour produced on immersing it in nitric acid of 1·32 sp. gravity, containing lower oxides of nitrogen. A reddish colour is also developed if New Zealand flax be immersed first in strong chlorine water and then in ammonia.

In machine-dressed *New Zealand flax* the bundles are translucent and irregularly covered with tissue. Spiral fibres can be detected in the bundles, but less numerous than with sizal. The bundles are flat, and numerous ultimate fibres project from them. In Maori-prepared *Phormium* the bundles are almost wholly free from tissue, and there are no spiral fibres.

769. *Hemp fibre* resembles flax, but has a mean diameter of about ·04 mm., and exhibits small hairy appendages at the joints.

With *manilla hemp* the fibrous bundles are oval, nearly opaque, and surrounded by a considerable quantity of dried-up cellular tissue composed of rectangular cells. The bundles are smooth, very few partly detached ultimate fibres are seen, and no spiral tissue.

770. *Sizal* forms oval fibrous bundles surrounded by cellular tissue; a few smooth ultimate fibres projecting from the bundles. Sizal is more translucent than manilla, and is characterised by the large quantity of spiral fibres mixed up in the bundles.

771. *Jute fibre* appears under the microscope as bundles of tendrils, each of which is a cylinder with irregularly thickened walls, the thickening often amounting to a partial interruption of the central lumen. The bundles offer a smooth cylindrical surface, to which fact the silky lustre of jute is due, and which is much increased by bleaching. By the action of sodium hypochlorite, the bundles of fibres can be disintegrated so that the single fibres can be more readily distinguished under the microscope. Jute is coloured a deeper yellow by aniline sulphate than is any other fibre, and responds strongly to the bromine and sulphite test (par. 754).

In examining fibres under the microscope the tissue should be cut up with sharp scissors, placed on a glass slide, moistened with water, and covered with a piece of thin glass.

772. Cellulosic Nitrates.

Nitric acid of 1·2 specific gravity has little or no action on cellulose in the cold, but when heated converts it into oxalic acid, oxy-cellulose, and other products.

With cold nitric acid of greater strength cellulose is converted into various nitro-substitution products or cellulosic nitrates, the constitution of which depends on the strength of the acid employed. Thus, with acid of moderate strength (1·45 specific gravity), mononitro-cellulose, $C_6H_9(NO_2)O_5$, is the chief product. With a mixture of equal volumes of strong sulphuric acid (1·85 specific gravity) and nitric acid of 1·42 specific gravity, dinitro-cellulose $C_6H_8(NO_2)_2O_5$ (par. 774.) is obtained; while if the strongest nitric acid be employed and strong sulphuric acid also added, the product is trinitro-cellulose, $C_6H_7(NO_2)_3O_5$,[1] (par. 779.)

All the cellulosic nitrates are soluble in strong caustic soda, undergoing partial saponification with formation of cellulose and sodium nitrate. Concentrated sulphuric acid displaces the nitric acid almost completely, even in the cold. By the action of reducing agents, such as ferrous chloride or acetate or potassium sulphydrate, the cellulosic nitrates are converted into cellulose even by digestion at the ordinary temperature. By boiling with a solution of stannous oxide in caustic potash, the nitro-celluloses are dissolved with conversion into cellulose, which is precipitated in flocks on neutralising the liquid (see also par. 784).

773. The *nitric peroxide*, NO_2, contained in specimens of nitrocellulose may be determined by reducing the substance with a ferrous salt, and measuring the nitric oxide, NO, evolved. (Champion and Pellet, *Comp. rend.*, lxxxiii. 707). A flask of 250 c.c. capacity is fitted with a caoutchouc stopper, through which pass two tubes, one leading to a pneumatic trough, while the other is a funnel-tube drawn out to a point and provided with a tap. The portion of this tube below the tap is filled with distilled water, while the funnel itself contains about 50 c.c. of a mixture of hydrochloric and sulphuric acids.[2] 0·5 gramme of the sample is placed in the flask together with about 5 grammes of ammonio-ferrous sulphate and 50 c.c. of water. The flask is then closed and the liquid boiled till the air is expelled. The acids in the funnel are then allowed to run slowly into the flask, when the

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[1] Curiously discrepant statements are made as to the action of solvents on the nitro-celluloses. Several chemists, in addition, deny that any more highly nitrated product can be obtained than corresponds to the formula $C_{12}H_{15}(NO_2)_5O_{10}$, or according to Vieille (*Compt. rend.*, xcv. 132) $C_{24}H_{29}(NO_2)_{11}O_{20}$, but Abel has shown that the preparations to which the first of these formulæ was ascribed had been imperfectly purified. On the whole, the balance of evidence seems in favour of the formula given in the text.

[2] Instead of the apparatus described in the text, that shown on page 148 (fig. 9) may be very conveniently employed.

boiling is continued as long as gas is evolved. The nitric oxide gas liberated is collected over soda solution, its volume measured, corrected for pressure and temperature, and calculated to weight.

The number of cubic centimetres of gas at 0° C. and 760 mm. pressure multiplied by 0·62693, gives the weight of nitrogen in milligrammes, which, multiplied by 1·72649, gives the equivalent weight of NO_2.

The nitric peroxide in gun-cotton may be determined by treating the sample with sulphuric acid and mercury, as in Crum's process of estimating nitrates in water. If conducted in a nitrometer, and the volume of gas compared with that yielded by a standard sample or nitre solution, as suggested by the writer (*Analyst*, v. 181), the process is very simple. A weighed quantity of the gun-cotton is placed in the cup of the nitrometer, and there dissolved in concentrated sulphuric acid. The resultant solution is then allowed to enter through the tap and is agitated with the mercury.

774. DINITRO-CELLULOSE, $C_6H_8(NO_2)_2O_5$, or $C_{12}H_{16}(NO_2)_4O_{10}$, constitutes the *pyroxylin* of the British Pharmacopœia, and differs from the mono- and the trinitro-derivatives by being soluble in a mixture of three measures of ether and one of rectified spirit, employed in the proportion of 48 c.c. to 1 gramme of pyroxylin. The solution thus obtained is known as collodion (*Collodium*, B.P.), and is a colourless liquid, which rapidly evaporates on exposure to the air, leaving a transparent film of dinitro-cellulose, insoluble in water or rectified spirit.

Pyroxylin is also soluble in acetone and in glacial acetic acid, and is precipitated in very voluminous flocks on diluting either of these solutions with water.

775. *Collodion* receives one of its principal applications in photography. It is now employed in the form of an emulsion for the preparation of dry plates. In addition to the constituents of the collodion, these emulsions generally contain argentic chloride, bromide or iodide, with the products of their formation from silver nitrate and the haloid compounds of potassium and sodium. On diluting the emulsion with water and filtering from the precipitated pyroxylin and insoluble silver salts, excess of argentic nitrate may be detected by the addition of hydrochloric acid to a portion of the filtrate, and excess of alkaline bromides, &c., by adding silver nitrate to the remainder of the solution. From the precipitate, after washing with alcohol, the pyroxylin may be dissolved out by digestion with ether-alcohol, and the insoluble silver salts dried, weighed, and further examined. Some collodion emulsions contain wood spirit and acetic acid, and various sensitisers or preserving

agents are liable to be present. Among those said to be more commonly used are gallic acid, pyrogallol, tannin solutions (such as tea and coffee infusions), cinchonine, cane sugar, glucose, glycerin, albumin, gelatin, and resins, especially colophony and shellac.

776. *Celluloid*, or "artificial ivory," is prepared on a large scale by treating pyroxylin with melted camphor or spirit of camphor, or by the simultaneous action of methyl or ethyl alcohol and camphor on pyroxylin. Various colouring agents and inert matters may also be present.

777. Celluloid cannot be caused to explode by heat, friction, or percussion. When brought in contact with flame it burns like paper, and continues to smoulder after the flame is extinguished, the camphor being distilled off with production of thick smoke, while the nitro-cellulose undergoes incomplete combustion.

778. Celluloid dissolves in warm moderately concentrated sulphuric acid, but is carbonised by the strong acid. It is readily soluble in glacial acetic acid, and on diluting the solution with water both camphor and pyroxylin are reprecipitated. It is rapidly soluble in warm moderately concentrated nitric acid (4 volumes of fuming acid to 3 of water), and is also dissolved with ease by a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood spirit behaves similarly. Ether-alcohol (3:1) dissolves both the nitro-cellulose and camphor, leaving the colouring and inert matters as a residue. The ash of celluloid ranges from 1·3 to 2·2 per cent. and the density from 1·310 to 1·393.

779. TRINITRO-CELLULOSE, $C_6H_7(NO_2)_3O_5$ or $C_{12}H_{14}(NO_2)_6O_{10}$, is obtained by treating cellulose in the cold with the strongest nitric acid (1·52 specific gravity) mixed with two or three times its bulk of concentrated sulphuric acid. The product is thrown into water and washed with scrupulous care. Trinitro-cellulose retains the form and appearance of the original cellulose from which it is prepared, but is found to have lost the property of depolarising light. It is somewhat hygroscopic, and becomes highly electrical when rubbed or pulled out briskly. Trinitro-cellulose is insoluble in water, alcohol, ether, and all mixtures of alcohol with ether. It is dissolved, however, by a mixture of ether, ammonia, and potash, and, according to some, by methyl or ethyl acetate (acetic ether), but this is most probably a mistake. In dilute acids it is insoluble.

Trinitro-cellulose is dyed by rosaniline, indigo, &c., in the same manner as are animal fibres.

Trinitro-cellulose, if dry, inflames when a light is applied, and burns very rapidly with a large, luminous, and wholly smokeless flame. When subjected to strong percussion it detonates with extreme violence, whether it be wet or dry.

780. *Gun-cotton*, when carefully made, consists almost wholly of trinitro-cellulose. It may be purified from foreign matters and lower nitro-derivatives by treatment with ether-alcohol (3 to 1).

781. THE ASSAY OF GUN-COTTON is sometimes of importance with a view of judging of its tendency to decompose. Pure trinitro-cellulose will keep indefinitely, but the presence of free acid, dinitro-cellulose, or fatty or waxy matters, renders it more or less unstable, and, therefore, unsafe.

782. *Free acid* may be detected by treating 20 grammes' weight of the gun-cotton with 50 c.c. of cold water. After twelve hours the water may be pressed out, filtered, and tested with litmus paper. If any trace of acidity be detected 25 c.c. of the liquid may then be titrated with decinormal caustic alkali. The remainder of the liquid may be employed to ascertain the nature of the free acid. If *sulphuric acid* be present, a small fragment of filter paper immersed in the solution will be charred on evaporating the liquid to dryness at 100° C. If *nitric acid* be the free acid, it may be detected by mixing the liquid with an equal bulk of pure sulphuric acid, cooling thoroughly, and placing a crystal of ferrous sulphate in the mixture. A brown tint will be developed in the neighbourhood of the crystal, if any nitric acid or nitrates be present.

783. *Dinitro-cellulose* and *foreign nitro-compounds* may be detected by treating 5 grammes of the sample, previously dried at 100° C., with 100 c.c. of a mixture of three parts of ether and one of rectified spirit. The mixture is shaken frequently during twelve hours, and is then rapidly filtered through loosely-packed glass-wool, the filtrate evaporated at a gentle heat, and the residue weighed.

784. *Unaltered cellulose* may be estimated by treating the gun-cotton left undissolved by the ether-alcohol with acetic ether, which dissolves the trinitro-cellulose and leaves the unchanged cotton. An alternative plan is to prepare a solution of sodium stannite by adding caustic soda to a solution of stannous chloride till the precipitate at first formed is just redissolved. The liquid thus obtained, when boiled with gun-cotton, dissolves the nitro-compounds, without affecting the unchanged cellulose.

785. The *nitric peroxide*, NO_2, contained in samples of gun-cotton may be determined as described in par. 773.

786. The *ash* of gun-cotton may be determined by melting some pure paraffin wax, at a gentle heat, in a platinum capsule, adding a known weight of the sample, and igniting from above. The mixture burns quite gently.

787. Some varieties of gun-cotton contain metallic *nitrates*, those of potassium and barium being usually employed. Potassium and sodium *chlorates* may also be found. Such admixtures may be removed by treating the sample with water, and recognised in the filtered solution by the methods of mineral analysis.

788. **STARCH.** $(C_6H_{10}O_5)n$.[1]

French—Fécule. *German*—Stärke.

Starch is found in cells in every part of plants, except in the top of the bud and the extremity of the rootlets. Although an especially characteristic product of the vegetable kingdom, starch-like substances are also met with in certain parts of animals.

789. Pure starch is a white, glistening, tasteless, and odourless powder. It is fixed in the air, and is not volatile or crystallisable. Ordinary air-dried starch contains about 18 per cent. of water, a proportion corresponding to the formula $C_6H_{10}O_5 + 2H_2O$.[1] When dried *in vacuo* the product contains $C_6H_{10}O_5 + H_2O$, and by heating to 100° or 110° C. in a current of dry air, anhydrous starch is obtained as a highly hygroscopic powder.

790. Starch is not dissolved without change by any known solvent.[2] It is quite unacted on by cold water, alcohol, or ether. When heated with water to a temperature varying according to the origin of the starch, it swells up and forms a paste. When the

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[1] Nägeli attributes to starch the formula $C_{36}H_{62}O_{31} + 5H_2O = 6C_6H_{10}O_5, H_2O$. Sachsse regards ordinary starch as a hydrate of the composition $C_{36}H_{60}O_{30}, H_2O + 12Aq$. Both these investigators ground their opinion on the amount of sugar produced by the action of acid, but Schulze has gone into the subject very carefully and fully confirms the empirical formula $xC_6H_{10}O_5$. Salomon obtained 111 per cent. of dextrose from potato starch, which points to a formula of $xC_6H_{10}O_5$; but from rice starch he could only obtain 107 per cent. of dextrose together with 4 per cent. of other products. Pfeiffer and Tollens attribute to starch the formula $C_{24}H_{40}O_{20}$, or $C_{24}H_{42}O_{21}$, and deduce this from the composition of the sodium and potassium compounds, which contain respectively 3·44 per cent. of Na, and 5·25 per cent. of K; but on the other hand, they consider dextrin and inulin to have the composition $C_{12}H_{20}O_{11}$, or $C_{12}H_{22}O_{11}$, so that the molecules of starch and inulin are not of the same size. The experiments of Brown and Heron point to the presence of C_{72} in the molecule of starch.

[2] According to Bungener and Fries (*Dingl. Polyt. Jour.*, ccxlix. 133) boiling water containing 1 per cent. of salicylic acid readily dissolves starch, forming a thick syrupy mass, which, on cooling, deposits "tabular crystals of starch." If finely ground barley be boiled for three quarters of an hour with 30 parts of water containing 1 per cent. of salicylic acid, and the hot opalescent liquid filtered, the solution will contain all the starch, which may be converted by dilute acid and determined in the usual way.

mixture is largely diluted with hot water almost perfect solution seems to occur, though it is doubtful how far this is really the case. The solution is strongly dextro-rotatory ($S_j = +222°$), and contains soluble starch. By heating with pure water, even under pressure, starch is not transformed into sugar.

791. When boiled with dilute acids starch is readily converted into a mixture of dextrin and maltose, prolonged treatment resulting in further hydrolysis and formation of dextrose (see p. 810). A solution of starch undergoes a similar change when treated with malt-extract, even in the cold, but solid starch is unaffected by malt-extract.

By treatment with cold nitric acid starch yields nitro-derivatives, but on heating with the reagent it is converted into oxalic acid and other products.

792. When treated with a solution of caustic potash or soda containing ½ to 1½ per cent. of the alkali, starch swells up enormously and forms a tenacious paste which is soluble in water, the solution yielding with cupric sulphate a blue precipitate, which does not blacken on boiling and is soluble in pure water. Ammonia does not gelatinise starch.

793. SOLUBLE STARCH or AMIDULIN is produced by boiling starch with water. A solution is thus obtained which may be rendered quite clear by addition of a little caustic alkali. It is strongly dextro-rotatory. Starch solution is one of the most perfect colloids known, and has a very high viscosity.

Soluble starch is not only obtained by boiling starch with water, but also by heating it to 100° C. with glacial acetic acid, or to 190° with glycerol. It is the first product of the action of dilute acids or malt-extract on starch. It is uncertain whether it is chemically or only mechanically distinct from the insoluble form of starch. Starch solution is perfectly neutral to litmus, but yields sparingly soluble precipitates with lime and baryta water. On exposure to the air, starch solution gradually decomposes, with formation of lactic acid.

794. Structure of Starch Corpuscles.

Starch occurs in plants in the form of minute granules, which generally possess a concentrically stratified structure, similar to that of an onion. These granules consist chiefly of a body called granulose, together with a closely allied substance known as amylo-cellulose or starch-cellulose, and water and traces of mineral matter. Starch-cellulose occurs in largest proportion in the outer layers of the granule, and probably constitutes the whole of the external coating. Owing to this protective coating, starch granules are wholly unacted on by cold water, as the internal granulose, though slightly soluble, is highly colloidal. When the outer layer of the granule is ruptured, as by grinding the starch with sand, water acts readily on it, and the liquid gives an intense blue colour with starch. By treating starch paste with malt-extract, the insoluble starch-cellulose may be obtained pure, and then is found to give only a dirty yellow colour with iodine. Saliva (owing to the ptyalin contained in it), and at a temperature of 50° to 60° C., pepsin, organic acids, very dilute hydrochloric or sulphuric acid, and a saturated solution of sodium chloride containing 1 per cent. of hydrochloric acid, all dissolve out the granulose and leave the amylo-cellulose intact. By boiling with water, starch-cellulose is mostly converted into soluble starch, leaving, however, a portion which obstinately resists the action of water, but is readily dissolved by dilute alkali. Amylo-cellulose differs from ordinary cellulose in being insoluble in Schweitzer's reagent. By repeated alternate treatment of potato-starch in the cold with very dilute alkali and acid, the cellulose may be removed, when the residue dissolves in hot water to form a perfectly clear solution. Solid starch corpuscles, when treated with iodine solution, are coloured intensely blue, the reagent readily penetrating the coating of cellulose and thus reaching granulose.

Young small corpuscles of starch appears to be invariably spherical, but as they grow older they may become lenticular, ovoid, or polygonal. The shape and size of the starch corpuscles are often highly characteristic of the plant by which they were produced, and this fact is frequently taken advantage of for identifying the presence of starch from particular sources.

795. Microscopic Identification of Starches.—When a sample is to be examined under the microscope for the identification of its starch, a minute quantity should be placed on a glass slide with the point of a knife. If in a powdered state, or readily reducible to powder, a preferable plan is to stir the sample with a dry glass rod, and tap the rod on the glass slide. A drop of distilled water or diluted glycerin (1 of glycerin to 2 of water) should then be added, and if the unpowdered structure be employed it should be broken up by careful mashing with the point of a knife. A glass cover is then put on, and any superfluous moisture removed by blotting paper. The specimen is now ready for observation. Somewhat oblique light should always be employed, and the power should vary from a $\frac{1}{2}$ to $\frac{1}{5}$ inch, using a B eye-piece furnished with a micrometer-scale, the value of the divisions of which have been previously ascertained. Too high a magnifying power should be avoided, especially in a first examination.

796. The points to be observed in the microscopic observation of starches are—(*a*) The shape and size of the granules. (*b*) The position and character of the *hilum*. (*c*) The concentric markings. (*d*) The appearance under polarised light. The two first observations are tolerably simple, but the examination for rings requires care, the markings being rarely visible without very cautious manipulation of the illumination and movement of the fine-adjustment, and then only in a few granules at the same time. Natal arrowroot and turmeric starches are almost the only two which show well-developed rings on nearly every granule. Wheat, on the other hand, shows no rings, even in the best light. When the hilum is situated near the centre of the granule, the rings are usually complete, but when the hilum is near one end of the granule only a segment of each ring is visible.

Although the size of starch-granules is a highly important character, it must be remembered that great variation occurs between individual granules, and that it is only the general or average size of the corpuscles which is usually recorded. Variation in size of the starch-granules is very marked in the case of the potato, in which the corpuscles range from 0·0025 of an inch in length down to less than 0·0002 (0·063 millimetre to less than 0·005).

Examination with polarised light, either with or without the use of a selenite plate, is a valuable auxiliary means of identifying starches, but many of the statements made in books, such as the black cross being observable in the case of certain starches only, must be considered as merely applicable to the precise conditions under which the observations referred to were made. With proper manipulation, all starches appear to show the black cross, and an ignorance of this fact has led many into error. Some starches show much more colour than others when examined under the polarising microscope. For observation of starches by polarised light it is often desirable to employ a highly-refracting mounting medium, and for such purposes water may be advantageously replaced by diluted glycerin, glycerin jelly, Canada balsam, oil of anise, carbon disulphide, &c.

W. H. Symons (*Pharm. Jour.*, [3] xiii. 237) has recorded a number of observations of the conditions under which starch-granules of different origins undergo tumefaction by the action of heat and dilute alkaline solutions. In some cases, the behaviour is sufficiently characteristic to serve as a means of differentiating the starches.

797. Much has been written on the microscopic appearance of starches, and some observers profess to be able to distinguish

starch of almost every origin. To the observer who has not made a special study of the morphology of starches, these distinctions are in many cases wholly unrecognisable, and as the minute points of difference are almost incapable either of description or delineation, the only safe method of discriminating starches is by a careful comparison of the sample with specimens of known origin and purity, making the observations under exactly similar conditions as to illumination, magnifying power, and mounting medium. These standard specimens should not be permanently mounted, but kept in an air-dry state, and a minute quantity mixed with water or other medium when required for use. As a rule, it is quite unnecessary to prepare the pure starches for comparison, a direct employment of the air-dried tissue answering every purpose.

798. Very complete tabular schemes for the recognition of starches by the microscope have been devised by Muter, (*Organic Materia Medica*, 2nd edition) and Vohl (*Ber.*, ix. 1660).[1] Of course, they in no way enable the observer to dispense with the requisite experience in observation, but they much facilitate the recognition by drawing the attention to the more characteristic features of the starches.

The following arrangement of starches, based on their microscopic appearance, is based on that of Muter. According to his method, the starches are arranged in five classes, having the following general characteristics:[2]—

I. The Potato Group includes such oval or ovate starches as give a play of colours when examined by polarised light and a selenite plate, and having the hilum and concentric rings clearly visible.

II. The Leguminous Starches comprise such round or oval starches as give little or no colour with polarised light, have concentric rings all but invisible, though becoming apparent, in many cases, on treating the starch with chromic acid, while the hilum is well marked, and cracked or stellate.

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[1] Hassall's work on *Food and its Adulterations*, and J. Bell's *Analysis and Adulterations of Food*, contains numerous woodcuts showing the microscopic character of starches.

Valuable articles on the identification of starches has been published by H. Pocklington (*Pharm. Jour.*, 3rd series, vol. iii. p. 663; vol. iv. p. 352; vol. vi. pp. 501, 662, 741), and J. W. Tripe (*Analyst*, vol. iv. p. 221).

[2] In order that mistakes may not be made in differentiating starches by the scheme, it is important to bear in mind that the appearances described apply to the following conditions of examination, namely, observation with oblique light; use of water as a medium, and a $\frac{4}{10}$ inch power, and B eye-piece; and, when polarised light is used, the use of a red-green selenite plate with diluted glycerin as a mounting medium.

III. **The Wheat Group** comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes the starches from wheat and some other cereals, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, &c.

IV. **The Sago Group** comprises those starches of which all the granules are truncated at one end. It includes some starches used for food, together with those from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. **The Rice Group** contains the starches all the granules of which are polygonal in form. It includes the starches from oats, maize, buck-wheat, rice, pepper, and ipecacuanha.

799. The following table gives further particulars respecting the microscopic appearance of the more important starches. The figures expressing the sizes are micro-millimetres (1–1000th millimetre), but they may be converted into ten-thousandths of an inch by multiplying them by the factor ·3937.

In the case of elongated starches, the figures expressing the size have reference to the mean of the longer and shorter diameters.

Origin of Starch.	Diameter in micro-milli-metres.	Characteristic Shape of Granules.	Other Characters.
Class I.			
Canna, or tous-le-mois.	47–132	Irregular oval, or oyster shaped.	Hilum annular and eccentric. Rings incomplete, very fine, narrow, and regular. Alkali develops lines and hilum. Well marked and regular cross with polarised light.
Potato.	Very variable; usually between 60 and 100.	Small granules, circular; the larger ovate, or oyster-shaped.	Hilum, a spot, generally near smaller end. Rings in larger granules numerous and complete. Very distinct cross towards smaller end, and brilliant colours with polarised light.
Maranta-arrowroot.	10 to 70; average 36	Somewhat ovoid or mussel-shaped, tending to triangular in larger granules. Sometimes irregular, with a nipple-like projection at same end as hilum.	Hilum, near one end, either circular or linear, and often cracked. Rings numerous and always visible, but not strongly marked. Well-defined cross towards larger end with polarised light, and brilliant colours.

Origin of Starch.	Diameter in micro-millimetres.	Characteristic Shape of Granules.	Other Characters.
Natal-arrow-root.	33 to 38	Broadly ovate, or occasionally circular, with irregular projections.	Hilum, a crack, eccentric. Rings very distinct under water.
Curcuma-arrowroot.	30 to 61	Resembles maranta. Elongated, or oval with irregular projections	Hilum, an eccentric dot or circle. Indistinct segments of rings. Heat or alkali deforms granules very irregularly.
CLASS II.			
Bean.	nearly uniform 34	Reniform or oval.	Hilum, stellate. Often becoming a longitudinal furrow. Smaller granules predominate.
Pea.	very variable 18 to 28	Reniform or oval.	Hilum elongated. Not distinguishable from bean in mixtures.
Lentil.	28	Reniform or oval.	Hilum elongated and very clearly defined. Rings moderately distinct.
CLASS III.			
Wheat.	very variable 2 to 52	Circular or nearly so, and flattened.	Chiefly of two sizes, large and very small. Shows a cross in glycerin with polarised light, but very slightly in water. Faint rings and colours are visible on the most elliptical granules.
Barley.	fairly uniform 13 to 39	Closely resembles wheat; some granules slightly angular, or elliptical.	Not certainly distinguishable from wheat in mixtures of the two.
Rye.	2 to 38	Closely resembles wheat.	A few granules show a three or four armed fissure extending nearly to the circumference.
Oat.	....	Large oval granules, showing polygonal divisions.	The compound granules break up by attrition into polygonal granules (see Class V.).
Acorn.	19	Circular or slightly oval.	Eccentric hilum developed by chromic acid.
CLASS IV.			
Arum.	14	Truncated with two facets.	Hilum eccentric.
Tacca-arrowroot.	9 to 19	Resembles tapioca.	Distinct hilum, linear and often starred. Very varied shape, often resembling maize, but has sharp angles.

Origin of Starch.	Diameter in micro-millimetres.	Characteristic Shape of Granules.	Other Characters.
Sago.	25 to 66	Ovate, or truncated oval.	Hilum, a circular spot or crack at convex end; faint rings. Well-defined cross, and often colours with polarised light. *Prepared sago* shows large oval depression; with polarised light characters less definite than the raw.
Tapioca.	8 to 22	Kettle-drum, or circular.	Hilum, a dot or short slit, nearly central. Well-defined cross and colours with polarised light. Characters of *prepared tapioca* are less definite.
CLASS V.			
Rice.	5 to 8	Pentagonal or hexagonal, occasionally triangular.	Angles sharply defined. Distinct hilum with a very high power, and cross visible in larger granules with polarised light.
Buckwheat.	5 to 20 depending on variety	Resembles oat and rice, but angles more rounded.	No rings, but distinct central hilum, as spot or star. Well-defined cross, with polarised light. Granules often compound.
Oat.	4 to 30	Triangular to hexagonal, a few small and round, or apple-pip shaped.	Rings and hilum invisible except under very high powers. Faint cross by polarised light.
Maize.	7 to 20	Circular to polyhedral, usually with rounded angles.	Hilum central, as a well-defined star or crack. Rings nearly invisible. Distinct cross and faint colours with polarised light.
Dari.	19	Small elongated hexagons.	...
Pepper.	½ to 5	Resembles rice, but majority decidedly smaller.	Shows hilum with very high power. Granules often in motion. Forms large compound granules of very irregular form.

800. ARROWROOT of commerce is the starch derived from plants of the genus *Maranta*, belonging to the order *Marantaceæ*. The most important member of the group is *Maranta arundinacea*, which is a native of the West India Islands and South America, but is now cultivated in Africa, Ceylon, and other hot

countries. Three other species of *Maranta* are recognised, namely, *M. allonyia* and *M. nobilis*, which grow in the West Indies, and *M. ramosissima*, a native of the East Indies. For trade purposes, arrowroot is distinguished by the name of the island or country producing it. Thus we have Bermuda, St. Vincent, Natal, Cape, Mauritius, and Rio arrowroots.

The starch corpuscles of the different species and varieties of *Maranta* differ considerably in their microscopic appearance (see Plate opposite), while certain varieties are closely simulated by the starches from plants other than the different species of *Maranta*. This is the case with the starch of *Curcuma angustifolia*, sometimes called East Indian arrowroot.

801. Arrowroot is liable to adulteration with a variety of cheaper starches, though the practice is now far less common than formerly. The principal starches which have been employed, either as substitutes for arrowroot or for mixing therewith, have been those of potato, sago, tapioca, curcuma, and tous-le-mois. Tacca and arum starches are also stated to have been employed, but they are not known at present in the English market.

The microscope affords the only satisfactory means of distinguishing maranta starch from the starches above mentioned, and even then the detection of certain admixtures is a matter of considerable difficulty. *Potato*[1] and *tous-les-mois* starches are distinguished by their large size, and regular and well-developed concentric rings, and potato, in addition, by the hilum being situated near the smaller end of the granules. *Sago*, *tacca*, *arum*, and *tapioca* are distinguished by the truncation of the granules. *Curcuma* starch closely resembles maranta, but the granules of the former are more irregular in size and shape, and also more pointed and transparent.

802. THE CEREAL STARCHES may be divided into two well-defined groups, wheat, barley, and rye starches being circular, or nearly so, while the starches of rice, maize, buck-wheat, and oat are polygonal.

803. THE LEGUMINOUS STARCHES present very close resemblances, and are generally indistinguishable from each other when in admixture.

804. *Determination of the Proportion of different Starches in admixture.*—The following is the best method, in the opinion of

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[1] Besides its microscopical appearance, potato starch is said to be distinguished from maranta starch in the following respects:—1. When mixed with twice its weight of strong hydrochloric acid, maranta starch produces an opaque white paste, while the paste produced by potato starch is transparent and jelly-like. 2. Potato starch evolves a peculiar and disagreeable odour when boiled with dilute sulphuric acid. 3. An acrid oil may be extracted from potato starch, but not from that of maranta.

the author,[1] for ascertaining the extent to which oatmeal is mixed with barley or wheat-flour, and is a type of the process to be employed in other cases. Genuine pearl-barley is ground finely in a mortar, and a series of standards made by mixing the flour with definite proportions of genuine oatmeal. Mixtures containing 5, 10, 15, 20, 30, and 40 per cent. of barley, respectively, will be found convenient in practice. The sample of oatmeal to be examined is thoroughly mixed, and 0·1 gramme weighed out and ground in an agate mortar, with a little water. When the mixture is perfectly smooth it is rinsed into a small conical glass, and diluted with water to 10 c.c. Two of the standard mixtures (say the 10 and 20 per cent. mixtures) are then treated in a precisely similar manner. A drop of the sample and one of each of the standards are then placed on glass slides and covered with thin covers. Care must be taken that the starches and water are thoroughly agitated, so that the drops taken shall be representative, and it is important that the drops themselves shall be of exactly the same size. These conditions are best ensured by immersing in the liquid a short piece of glass tube drawn out to a fine point, blowing down it so as to mix the sample thoroughly by means of the air-bubbles expelled, and then allowing a drop of the liquid to fall from the orifice on to the glass slide. The same tube is then employed to take drops of the standard mixtures. The cover glasses must all be of equal size, and sufficiently large to take up the whole of the drop, as none of the liquid must be removed The slides being prepared, the number of barley granules visible in twelve successive fields is noted. The standards are then similarly observed, the operation being repeated until a standard mixture is found, the barley granules in twelve fields of which are equal or nearly equal in number to those counted in the sample. The proportion of wheat or barley in the sample will then be approximately the same as that in the standard it agrees with.

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[1] Dr James Bell, from whose little book on *Foods* (part ii.) much of the information in the text on arrowroot and other starches has been gathered, gives the following method for estimating starches in admixture :—"The sample is first rubbed in a mortar and passed several times through a sieve. A small quantity, say 0·05 of a grain, is then weighed out and placed on a glass slide, where it is worked into a thin paste with about two drops of water. A thin covering glass, measuring about 1½ inch by 1 inch, is then placed over the paste, and moved about the slide until the paste is equally distributed and all under the covering glass. With a ¼-inch objective, the number of granules is counted in nine fields, as fairly as possible representing the entire slide. The process is repeated till a correct idea of the composition of the sample is obtained. Standard mixtures approximately representing the sample are made up and treated in exactly the same way, and from a comparison of the results the percentage of foreign starch is computed."

805. Detection and Determination of Starch.

For the detection of starch existing in the *solid* state, no method is so good as the microscopic recognition of the corpuscles, the origin of which may usually be identified in the manner already described. The microscopic examination may be advantageously supplemented by adding a drop of iodine solution to the slide, when each of the true starch granules will assume a blue colour, which renders their recognition easy. In some cases, as when roasted coffee is mixed with beans or acorns, the microscopic detection of the starch becomes difficult, but may still be effected in the following manner:—The coffee is boiled with water for a few minutes, and the solution is decanted or filtered from the insoluble matter. The liquid is next thoroughly cooled, and cold dilute sulphuric acid is added. A solution of potassium permanganate is then gradually added till the brown colour is nearly or entirely destroyed, when the decolorised liquid is tested with iodine. A blue colour is obtainable in this way with coffee containing only 1 per cent. of roasted acorns.

Sometimes it is desirable to remove the colouring matter from the solid substance before examining it for starch. If cold water fail to effect this, alcohol should be tried, and subsequently other solvents. The cases are rare, however, in which the starch cannot be observed microscopically after successive treatments of the substance with cold water and alcohol.

806. In *aqueous solution*, starch yields a precipitate with ammoniacal acetate of lead having a composition represented approximately by the formula $C_{12}H_{18}Pb_2''O_{11}$. Tannin gives a white precipitate with starch solution, disappearing on warming and re-appearing as the liquid cools. Soluble starch is completely precipitated by adding alcohol to its aqueous solution.

807. The most characteristic reaction of starch solution is the violet or indigo-blue coloration which it gives with iodine. The coloured body does not appear to be a definite compound of starch with iodine, and hence is best called iodised starch. The best form in which to employ the reagent is as a very dilute solution of iodine in iodide of potassium. The starch solution should be perfectly cold. On heating the liquid it is decolorised, but on cooling the blue colour is restored, though not with the same intensity as before. In employing the reaction as a test for starch it is necessary to remember that it is only produced by *free* iodine. Hence any free alkali should be neutralised by cautious addition of cold dilute acid, and any reducing or oxidising agent got rid of if possible. The best way of testing for starch is to add the iodine solution gradually to the slightly acid liquid until either

a blue colour appears or the liquid remains permanently coloured yellow by the free iodine. If the latter effect is produced and yet no blue coloration is obtained no starch can be present.

808. The only organic body liable to interfere when the test is performed in the foregoing manner is erythro-dextrin, which itself produces an intense reddish-brown coloration with iodine, which is apt to mask a feeble starch-reaction. The affinity of iodine for starch is, however, greater than its affinity for erythro-dextrin, and hence if a very little iodine solution be employed the blue colour due to starch will alone be developed, the brown coloration becoming apparent on a further addition of the reagent. By cautiously adding very dilute ammonia, or gradually heating the liquid, the brown colour can be destroyed while the blue remains.[1]

809. THE DETERMINATION OF STARCH is effected in different ways according to the nature of the substance in which it occurs. In wheat-flour a convenient but very rough plan is to place a weighed quantity of the sample in a sieve, and allow a stream of water to trickle over it, kneading well all the time. When the water runs away clear, it is allowed to stand, and, when the starch has all settled out, the water is poured off and the deposited starch collected, dried at 110°, and weighed.

810. In plant-products, such as wheaten-flour, oatmeal, cocoa, &c., the determination of starch may be effected as described in par. 845. The conversion of the starch into dextrose by boiling with dilute acid (par. 507) and estimation of the resultant glucose by Fehling's solution, is a process giving fairly good results if carefully conducted, but there is a danger of the estimation being low from incomplete conversion to dextrose or the formation of secondary non-reducing bodies. 10 parts of dextrose thus found correspond to 9 parts of anhydrous starch. The change to dextrin and maltose is easily made, and may be effected either by heating the starch with dilute acid or by the action of diastase. When very accurate estimations of starch are required this is probably the best process to employ. It is applicable to all the cereals, raw as well as malted, and is conducted by C. O'Sullivan (*Jour. Chem. Soc.*, xlv. 1) in the following manner:—A fair sample of the grain is taken and 5·1 grammes weighed roughly and ground to a fine flour in a clean coffee-mill. 5 grammes of the powder is placed in a flask of about 120 c.c. capacity thoroughly wetted with rectified spirit, and 25

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[1] Neither the brown colour of a solution of iodised erythro-dextrin nor the blue of iodised starch shows any absorption bands when examined by the spectroscope. According to Bondonneau, iodised starch has a definite composition represented by the formula $(C_6H_{10}O_5)I_5$.

c.c. of ether added. The flask is corked and agitated occasionally, and after a few hours the ether is decanted through a filter and the residue washed by decantation with three or four fresh quantities of ether. To the residue 80 to 90 c.c. alcohol, specific gravity 0·90, are added, and the mixture kept at 35° to 38° C. for a few hours with occasional shaking. The alcoholic solution, when clear, is decanted through the filter used in filtering the ethereal solution, and the residue washed a few times by decantation with alcohol of the strength and at the temperature indicated. The residue in the flask, and any little that may have been decanted on to the filter, is then treated with about half a litre of cold water. In about twenty-four hours the supernatant liquid becomes clear, when it can be gradually decanted through a filter. The solution filters bright, but, in the case of barley and oats, exceedingly slowly at times; the malted grains, as well as wheat, rye, maize, and rice, yield solutions requiring no excessive time to filter. The residue is repeatedly washed with water at 35° to 38°, but this treatment does not completely free barley and oats from α-amylan, which body dissolves with the greatest difficulty at this temperature. The residue is then transferred to a 100 c.c. beaker, and the portion adhering to the filter washed off by opening the filter-paper on a glass plate and removing every particle by means of a camel's hair brush, cut short, and a fine-spouted wash-bottle. When the transference is completed, the beaker, which should not now contain more than 40 to 45 c.c. of the liquid, is heated to 100° for a few minutes in the water-bath, care being taken to stir well when the starch is gelatinising to prevent "balling" or unequal gelatinisation. After this the beaker is cooled to 62° to 63°, and 0·025 to 0·035 gramme diastase[1] dissolved in a few c.c. water, added.

On keeping the liquid at 62° to 63° for a short time, the starch is completely converted into maltose and dextrin, and a drop of

[1] The diastase employed is prepared as follows :—2 or 3 kilogrammes of finely-ground pale barley-malt are taken, sufficient water added to completely saturate it, and when saturated to slightly cover it. When this mixture has stood three or four hours, as much of the solution as possible is pressed out by means of a filter-press. If the liquid is not bright it must be filtered. To the clear bright solution rectified spirit is added as long as a flocculent precipitate forms, the addition of the alcohol being discontinued as soon as the supernatant liquid becomes opalescent or milky. The precipitate is washed with alcohol of 0·86 to 0·88 specific gravity, dehydrated with absolute alcohol, pressed between cloth to free it as much as possible from that liquid, and dried *in vacuo* over sulphuric acid, until the weight becomes constant.

Prepared in this way the substance is a white, friable, easily soluble powder, retaining its activity for a considerable time. The preparation usually sold as diastase is useless for this work.

the solution no longer gives a blue coloration with iodine, but it is desirable to continue the treatment for about an hour after the disappearance of the starch, as the solution then filters more readily. The liquid is then heated to boiling for ten minutes, and filtered, the residue being carefully washed with small quantities of boiling water. The filtrate is cooled, and made up to 100 c.c. and the density observed. The maltose is then determined by Fehling's solution, and the dextrin deduced from the rotatory power of the solution. The maltose found, divided by 1·055, gives the corresponding weight of starch, which, added to the dextrin found, gives the total number of grammes of starch represented by 100 c.c. of the solution.[1] The sum of the dextrin and maltose found directly ought to agree fairly well with the total solid matter estimated from the density of the solution, after making allowance for the weight of diastase employed.

811. The foregoing process, involving as it does the preparation of diastase, is not always a convenient one to employ, and in such cases the following modification will be found of service, though it does not aim at so high a degree of accuracy as the method prescribed by O'Sullivan. Any fat and essential oil having been removed by treatment with ether, the substance is treated with a saturated solution of salicylic acid in cold water. This will dissolve alkaline salts, sugar, dextrin, &c. The liquid is filtered, and the residue washed with decinormal caustic soda (4 grammes NaHO per litre) to remove salicylic acid and albuminoids. The residue is rinsed off the filter with warm water, the liquid heated to boiling while constantly stirred, so as to gelatinise the starch, and the product treated with a known measure of recently-prepared and filtered cold infusion of malt, of which the specific gravity has been previously ascertained. The mixture is kept at a temperature of about 60° to 63° C., with occasional stirring, until a drop taken out with a glass rod and added to a drop of diluted iodine solution on a porcelain plate shows no blue or brown coloration. The solution is then filtered, made up to a definite volume, and its specific gravity accurately ascertained. From the excess of the

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[1] In very accurate experiments, it may be well to estimate the α-amylan present in the solution. For this purpose, 75 c.c. of the above solution should be evaporated to about 30 c.c., cooled, and 60 c.c. of rectified spirit added. A few drops of hydrochloric acid are then added, and the opalescent liquid stirred, when a flocculent precipitate will probably be produced. This is allowed to subside and the clear supernatant liquid is decanted off. The residue is then washed with alcohol of 0·86 specific gravity, dehydrated by treatment with strong alcohol, and collected on a tared filter. It is then dried *in vacuo* over sulphuric acid, and afterwards in dry air at 100° C., being subsequently weighed.

density over water is subtracted the density due to the infusion of malt used, allowance being made for the increased volume of the liquid, when the difference represents the density due to the starch dissolved, and this number divided by 4·096 (=3·95 × 1·037) gives the number of grammes of starch in each 100 c.c. of the solution.[1]

812. For technical purposes it is sometimes desired to determine the proportion of starch existing in potatoes. This can be done in a rough and ready manner by ascertaining the specific gravity of the tuber. The unpeeled potatoes, freed from dirt, are placed in a solution of salt, which is then diluted with water till some of the individual tubers sink, while others just float. The density of the saline solution, as ascertained by a hydrometer, is then equal to the average specific gravity of the potatoes. Another method consists in taking 5 kilogrammes of the potatoes, and then weighing in water. The weight in water divided into the original weight in air gives the specific gravity. Tables have been compiled for ascertaining the percentage of starch from the specific gravity of the potatoes. The most complete table is that of Heidepriem (*Jour. Chem. Soc.*, xxxii. 233), for which may be substituted the following formulæ, in which W is the weight of 5 kilogrammes of potatoes immersed in water.

$$(W-285)\ {\cdot}052+\ 7{\cdot}13=\text{percentage of starch; and}$$
$$(W-285)\ {\cdot}052+14{\cdot}35=\text{percentage of solid matter.}$$

813. **Commercial Starch** is usually obtained from wheat, rice, maize, or potatoes. This statement applies simply to the varieties of starch sold under that name, for arrowroot, tapioca, sago, and farinaceous foods often consist of starch in a condition of considerable purity. The origin of a specimen of starch can usually be ascertained by observing its appearance under the microscope (par. 795).

Commercial starch is generally very pure, though occasionally it may contain traces of vegetable fibre and of albuminoid matters.

Starch often occurs in commerce in irregular elongated lumps, having a basaltic-like structure. This appearance is especially characteristic of wheat starch, the small admixture of gluten causing the granules to cohere. An admixture of potato starch with wheat starch prevents agglutination, and tends to cause the starch to fall to powder.

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[1] Thus, suppose 10 grammes of the sample be taken, and, after treatment with ether and salicylic acid and soda solutions in the manner described, the residue be treated with 50 c.c. of water and 5 c.c. of infusion of malt of 1060 sp. gravity; the liquid being subsequently made up to 100 c.c. and found to have a density of 1033. Then, the correction due to the malt-extract will be $\frac{(1060-1000)\times 5}{100}=3$; this, subtracted from the difference between the density of the solution and that of water (1033 − 1000 = 33) leaves 30 as the excess-density caused by the solution of the starch of the sample; and this figure, divided by 4·096, gives 7·324 grammes per 100 c.c., or in the 10 grammes taken; or 73·24 per cent. of starch in the sample.

The *ash* of commercial starch should be very trifling in amount. Its determination serves to detect any mineral additions.

814. The proportion of *water* in air-dried starch averages about 18 per cent., but is liable to considerable variation. It may be determined by drying the starch in a vacuum over sulphuric acid, till constant, and then in a current of dry air at 100°. Saare has described a method of approximately estimating the water in potato starch, which consists in placing 100 grammes of the sample in a 250 c.c. flask, filling the flask to the mark with water at 17·5° C., and observing the weight of the contents. There is no occasion to employ the large quantities of starch and water recommended by Saare. He gives a table (*Jour. Soc. Chem. Ind.*, iii. 527) by which the proportion of water is directly shown, but the following rule may be employed instead:—From the weight of the starch and water contained in the bottle subtract 250, and divide the difference by 0·3987, when the dividend will be the percentage of starch in the sample. This instruction applies to the quantities of starch and water prescribed by Saare, but the following is a more general expression of the rule:—

$$\frac{\text{Contents of bottle in grammes } \textit{minus} \text{ capacity of bottle in c.c.}}{\cdot 3987} = \left\{\begin{array}{l}\text{the number of grammes of}\\ \text{anhydrous starch in weight}\\ \text{of sample taken.}\end{array}\right.$$

815. DEXTRIN.

Amylin. $(C_6H_{10}O_5)_n$.

Dextrin is a product obtained by treating starch or amylaceous bodies in certain ways. The following modes of treatment cause a formation of dextrin:—

(*a*) By heating starch or flour to a temperature varying from 210° to 280° C., till it acquires a yellow or brownish colour. The change is greatly facilitated by moistening the starch with dilute nitric acid, and then slowly drying the paste and heating it for some time to about 110° to 150° C.

(*b*) By boiling starch with dilute sulphuric acid till the cooled liquid no longer gives any coloration with solution of iodine.

(*c*) By treating gelatinised starch with warm water and a small quantity of malt-extract.

Process *a* is largely employed for the manufacture of solid dextrin, which is known in commerce by the name of British gum, gommeline, starch-gum, &c. Processes *b* and *c* result in a simultaneous formation of maltose, as described in par. 615; *b* is used for the preparation of commercial glucose, and *c* is the reaction which takes place in mashing malt for the manufacture of beer.

816. Several, and not impossibly many, varieties of dextrin exist, all being apparently formed by the breaking up of the highly complex starch molecule by treatment with dilute acids or ferments. There is no ready method of distinguishing the different varieties with certainty, except that one kind, or possibly class, of dextrin gives a reddish-brown colour with solution of iodine, while the other kind or class produces no coloration. The erythro-dextrin, the kind giving the brown colour with iodine, is an intermediate product of the formation of achro-dextrin from starch.[1]

The best method of applying the iodine reaction as a test for erythro-dextrin is to divide a very weak solution of the iodine in iodide of potassium into two parts, and place the slightly yellow liquid in adjacent test-tubes or glass cylinders. On then adding the solution to be tested to one, and an equal measure of water to the other, any brownish coloration will be readily observed. In presence of starch, the blue colour is apt to obscure the brown tint produced by the erythro-dextrin. This may be avoided to some extent by employing the iodine solution somewhat in excess, so as to get a full development of the brown colour.

817. Pure dextrin is a white amorphous solid. It is tasteless, odourless, and non-volatile. Dextrin is very deliquescent, and dissolves in an equal weight of cold water to form a syrupy and strongly dextro-rotatory liquid[2] which is miscible with 1½ measures of proof spirit. By strong spirit, if used in sufficient quantity, dextrin is completely separated from its aqueous solutions.

818. Cold concentrated sulphuric acid dissolves dry dextrin without colour, but charring takes place on warming. By boiling with dilute acids, dextrin yields maltose and ultimately dextrose (see par. 508).[3] Hot nitric acid of 1·35 specific gravity converts dextrin in part into oxalic acid, whereas the natural gums yield mucic acid under similar conditions.

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[1] According to Musculus and Meyer (*Jour. Chem. Soc.*, xl. 570), erythro-dextrin is a variety of soluble starch. They obtained the intense red colour which characterises erythro-dextrin when a half per cent. solution of soluble starch was added to a solution of a higher dextrin which gave a pure yellow-brown colour with iodine.

[2] $S_D = 200$ and $S_j = 222$. These corrected figures for the specific rotation of dextrin are somewhat higher than those given in previous paragraphs.

[3] According to Musculus and Meyer the re-conversion of dextrose into a variety of dextrin can be effected by dissolving the glucose in strong sulphuric acid, heating the mixture to 60° till it becomes brown, and then throwing it into a large quantity of absolute alcohol. On boiling the product with water a yellow amorphous mass is formed having the characters of dextrin.

819. Dextrin is distinguished from starch by its solubility in cold water; from soluble starch by yielding no blue colour with iodine when tested as described in par. 808, and no precipitate with baryta water; from maltose and dextrose by not reducing Fehling's solution; from starch, soluble starch, gelatin, and egg-albumin by not yielding a precipitate with tannin; from albumin, by not being coagulated by heat or mineral acids.

820. Dextrin is separated from starch and cellulose by solution in cold water; coagulable albuminoids may then be separated by raising the faintly acid solution to boiling. An ammoniacal solution of acetate of lead added to the cold and dilute liquid is stated to precipitate the dextrin, leaving the sugar in solution. The precipitate may be dried at 100° C., and is said to have the formula $PbO,C_6H_{10}O_5$. Another method consists in precipitating the dextrin by means of a large proportion of alcohol, washing the precipitate with rectified spirit, and drying it at 110° C. After weighing, the dextrin should be ignited, and the resultant ash deducted from the total weight obtained.

The proportion of dextrin present in a solution also containing maltose and dextrose may be determined by observing the rotatory action of the liquid, together with its specific gravity, and reducing action on Fehling's solution. Further information on the determination of dextrin will be found in pars. 508, 548 to 554, 635 to 638, 696 to 705, and 728.

821. Commercial Dextrin.

Commercial dextrin, or "British gum," is now manufactured extensively by moistening starch or flour with a mixture of dilute nitric and hydrochloric acids, and then exposing it to a temperature of 100° to 125° C. Either nitric or hydrochloric acid singly may be substituted for the mixture, or oxalic acid may be employed.

822. Commercial dextrin is a white, yellowish, or light brown powder. It consists largely of erythro-dextrin, and hence its aqueous solution gives a brown coloration with iodine, unless this reaction is obscured by the blue colour produced by a considerable proportion of soluble *starch*. For most purposes this admixture is unobjectionable, provided that it does not exceed 12 or 15 per cent. *Unaltered starch* may be recognised by the microscope and its insolubility in cold water. Reducing *sugars* (maltose) are nearly always present in commercial dextrin, and may be detected and estimated by Fehling's solution.

Many mixtures of starch and dextrin are employed as thickening agents in calico-printing, &c. "Gloy" consists essentially of farina mixed with a solution of magnesium chloride.

Dextrin syrups are largely employed by confectioners. Their examination is described in par. 691 *et seq.*

The method of distinguishing commercial dextrin from gum arabic is described in par. 837.

823. GUMS.

French.—Gommes. *German.*—Gommi.

Gums are a peculiar class of bodies occurring in the juices of plants. They are perfectly non-volatile, have little or no taste, are uncrystallisable, and eminently colloidal. These characters render their purification very difficult, and hence but little is known of their chemical relationships. Many of them appear to be true isomers of starch, but others have a different composition. For convenience, various pectous bodies are classed with the gums.

The analytical characters of the gums as a class are indicated by the following facts, which are also applied to their separation from similar bodies.

824. Gums are either soluble in, or swell up in contact with, cold water, a character which distinguishes them from starch, cellulose, and resins. They differ from the sugars by being incapable of fermentation by yeast, and from the sugars and resins by their insolubility in alcohol. From dextrin the gums soluble in water are distinguished by their lævo-rotatory power and acid reaction, and by yielding mucic acid by treatment with moderately concentrated nitric acid.[1] Reichl and Breinl state that arabin and bassorin are distinguishable from dextrin by the blue flocculent mass they yield when heated with hydrochloric acid and orcinol, dissolving in alcoholic potash to form a violet solution showing a green florescence. Fragments of wood, containing only traces of wood-gum, when boiled with hydrochloric acid and orcinol show the reaction quite distinctly. From erythrodextrin and starch the gums differ by giving no colour with solution of iodine, and from albuminoids they are distinguished by not yielding ammonia when ignited with soda-lime.

825. The gums having been very imperfectly studied, it is impossible to arrange them with any degree of scientific accuracy. They may, however, be conveniently classified according to their behaviour when treated with cold water and dilute acids. Thus the gums of which gum arabic is the type are dissolved by cold water, and are not readily precipitated by acids. Pectin forms a jelly when its aqueous solution is faintly acidified, while gum tragacanth merely swells up when treated with cold water, without undergoing notable solution.

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[1] According to Nägeli and Cramer, quince-mucilage yields no mucic acid by treatment with nitric acid. Mucic acid gives a crimson coloration when treated with concentrated sulphuric acid.

Name of Gum.	Chief Source or Mode of Formation.	Characteristic Properties.
Arabin, ...	Gum arabic, and the soluble portion of other gums.	Formula complex. *Lævo*-rotatory. (See also page 351.)
Metarabin, . . Pararabin, . .	Roots of carrot, beet, &c.	Insoluble in water. Metarabin is converted into arabin by treatment with dilute *alkali*. Pararabin undergoes a similar change by treatment with *acids*.
Cerasin, ...	The insoluble part of cherry-tree gum, peach-gum, &c.	Said to be metagummate of calcium. By long-continued boiling with water it yields arabin.
Gelose, ...	China and Ceylon moss, Japan isinglass (*Gelideum corneum*).	Said to contain $C_6H_{10}O_5$. Feebly lævo-rotatory. Forms a jelly with 500 times its weight of water. Heating with water under pressure, or boiling with dilute acids (including acetic), destroys power of gelatinising, and forms bodies reducing Fehling's solution. Heated with nitric acid gelose yields mucic and oxalic acids.
Dextran or Viscose. .	Unripe beet-root; molasses; mucic and lactic fermentations.	White friable substance, insoluble in alcohol. Dextro-rotatory ($S_D = +223°$). Yields dextrose and dextrin when boiled with dilute acid. Formula $C_6H_{10}O_5$.
Lævulan, . . .	Beet-root molasses.	$C_6H_{10}O_5$. White amorphous. Soluble in hot water, gelatinising on cooling. Lævo-rotatory ($S_D = -221°$). Yields lævulose when boiled with dilute acid. Forms mucic acid on treatment with nitric acid.
Wood Gum, . . .	Various woods.	Insoluble in cold water or ammonia, but dissolves in 50 parts of hot water, and readily in caustic soda, forming lævo-rotatory solution. With dilute acid it yields a reducing but unfermentable sugar.
Carragheenin, . . .	Irish moss (*Chondrus crispus*).	
Pectin, ...	By the action of a natural ferment on pectose, an insoluble body existing in unripe fruits. Exists ready-formed in ripe fruits, and very largely in Irish moss.	Optically inactive. Soluble in water, the solution gelatinising on adding either acid or alkali. Also precipitated by alcohol, but not by neutral lead acetate till after boiling the solution, by which parapectin is formed. By boiling with acid, forms metapectin, which is acid to litmus and precipitated by barium chloride. By treatment with bases all varieties of pectin yield pectates, which, on addition of hydrochloric acid, give insoluble pectic acid.
Bassorin or Tragacanthin,	Gum bassora and gum tragacanth.	Insoluble in cold water, but swells up. By prolonged action of boiling water, yields pectin. By boiling with very dilute hydrochloric acid, yields pectic acid, insoluble in cold water. (See page 355.)
Vegetable mucilages, .	Occur largely in linseed, marsh-mallow root, quince seed, elm bark, &c.	Yield dextro-rotatory reducing sugars and dextrinoid bodies (and sometimes cellulose) by boiling with dilute acids. Very little understood.
Algin, ...	Various seaweeds (*Laminaria*, *&c.*).	Soluble in cold water, forming very viscous solution which does not gelatinise on cooling; precipitated by hydrochloric acid, alcohol, and many salts, including calcium chloride, but not magnesium chloride. Not precipitated by mercuric chloride or tannin. Contains nearly 4 per cent. of nitrogen (*Jour. Soc. Chem. Ind.*, iii. 297.)

826. The foregoing table shows the leading properties of the principal natural gums and pectous matters. Gum arabic and gum tragacanth are described more fully in the following sections.

827. **Gum Arabic.**—Gum Acacia.

Gum arabic is the dried exudation from the bark of various species of *Acaciæ*. Strictly speaking, "gum arabic" is the generic name, "gum acacia" being properly limited to the superior qualities employed in medicine. These are largely obtained from the Soudan. The finest kind of gum arabic occurs in commerce in lumps of various sizes, colourless, and full of minute cracks. Gum Senegal forms yellowish or reddish lumps, often of the size of a pigeon's egg, and not having the minute cracks of the better varieties. It is less readily soluble than true gum arabic, and its solution soon becomes very dark in colour.

828. Gum arabic consists essentially of the calcium salt of arabin or arabic acid, which may be obtained pure by dialysing a solution of the gum previously acidulated with hydrochloric acid. The colloid liquid thus obtained is *lævo*-rotatory, and is not precipitated by pure alcohol, but is thrown down if a trace of any acid or salt be present. After being evaporated to dryness and heated to 100° C., the arabin does not re-dissolve, even in hot water, but swells up into a gelatinous mass, which gradually dissolves on treatment with soda, or lime or baryta water, yielding a liquid indistinguishable from the aqueous solution of ordinary gum arabic.

829. ARABIC ACID or Arabin has been recently studied by C. O'Sullivan, who has disproved the formula $C_{12}H_{22}O_{11}$ commonly attributed to it. He finds it to contain $C_{89}H_{142}O_{74}$, the calcium salt having the formula $C_{89}H_{142}O_{74},CaO$, so that the free acid appears to be really an anhydride. By heating with dilute sulphuric acid, arabic acid is split up into a series of dextrorotatory glucoses or arabinoses, of which at least four species have been already recognised, and a whole series of acids, called arabinosic acids, having a smaller number of carbon atoms than arabic acid itself[1] (*Jour. Chem. Soc.*, xlv. 41).

830. Most varieties of gum arabic—including the Levantine, Sennaar, East Indian, and Senegal—are lævo-rotatory, but Australian gum is often optically inactive, while Gedda gum is dextro-

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[1] The first change by the action of sulphuric acid may be assumed to be as follows:—

$$C_{89}H_{142}O_{74} + H_2O = C_6H_{12}O_6 + C_{83}H_{132}O_{69}.$$

By further action of sulphuric acid, O'Sullivan obtained evidence of the existence of the following series of acids, differing from each other by $C_6H_{10}O_5$, or a rotatory. Chemically, these gums are analogous to the dextrorotatory varieties.

The inferior qualities of gum contain a small percentage of a reducing sugar, which may be removed by treatment with alcohol.

The specific gravity of air-dried gum arabic ranges from 1·35 to 1·49, but when completely dried at 100° it loses about 13 per cent. of water, and the density increases considerably.

831. Gum arabic has a very faint odour and a mucilaginous insipid taste. It dissolves slowly in about twice its weight of water, forming a thick transparent mucilage of acid reaction.[1] Gum is slightly soluble in dilute spirit, but quite insoluble in liquids containing more than 60 per cent. of alcohol, and is precipitated from its aqueous solution on addition of a large proportion of spirit.

832. The aqueous solution of gum arabic is not precipitated by

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multiple of this group, which appears to be split off from the molecule, and undergoes conversion into glucose by hydrolysis:—

Acid.	Formula.	S_j.	BaO in Barium Salt.
Arabic	$C_{89}H_{142}O_{74}$	−27	6·00 per cent.
α-Arabinosic	$C_{83}H_{132}O_{69}$	...	6·41 ,,
β-Arabinosic	$C_{77}H_{122}O_{64}$	...	...
γ-Arabinosic	$C_{71}H_{112}O_{59}$	...	7·42 ,,
θ-Arabinosic	$C_{41}H_{68}O_{37}$	inactive	11·71 ,,
ι-Arabinosic	$C_{35}H_{58}O_{32}$	...	13·38 ,,
κ-Arabinosic	$C_{29}H_{48}O_{27}$	...	15·59 ,,
λ-Arabinosic	$C_{23}H_{38}O_{22}$	...	18·68 ,,

From some lævo-rotatory specimens of gum arabic O'Sullivan has isolated arabic acids having an optical activity varying from $S_j = -22°$ to $S_j = -34°$, the value of S_j for the normal arabic acid containing C_{89} being −27 to −28°. The less optically active acids yielded barium salts containing from 6·5 to 6·7 of BaO, and hence probably contain α-arabinosic acid; while, on the other hand, the fractions of highest opticity gave barium salts containing only 5·6 to 5·8 per cent. of BaO, suggesting the probable presence of an acid of the formula $C_{96}H_{152}O_{80}$.

The glucoses formed by the action of dilute sulphuric acid on arabic acid had the following reducing and rotatory powers:—

	α-arabinose.	β-arabinose.	γ-arabinose.	δ-arabinose.
K	...	110	100·5	81 to 82.
S_j	above +140	+111	+91	+79 to 81.

[1] Suakim gum, which is quite brittle, is often not wholly soluble in water, but yields with it a pasty mass of rather strong acid reaction, depositing, when diluted with water, transparent globules, said to consist of metagummic acid which may be rendered soluble by adding a little potash or lime-water.

neutral lead acetate, but with the basic acetate it forms a white jelly. Its solution is also precipitated by potassium or sodium silicate, borax, ammonium oxalate, mercuric chloride, and ferric salts.

833. The proportions of mucic acid obtainable from the different varieties of gum by oxidation with nitric acid have been determined by Kiliani (*Ber.*, xv. 34), who found amounts varying from 14·3 per cent., from a sample of East Indian gum, to 38·3 per cent. from an Australian sample.[1]

834. By adding a saturated solution of aluminium sulphate to one of gum arabic, the adhesive properties of the latter are said to be much increased, owing to the formation of aluminium arabate, while calcium sulphate is gradually deposited.

835. The presence of gum arabic in a solution presents the formation of a number of characteristic precipitates (Lefort and Thibault, *Pharm. Jour.*, [3] xiii. 301), a fact which is of importance in toxicological researches. Thus, in presence of gum arabic, dilute solutions of mercury, lead, copper, silver, iron, arsenic, &c., do not give precipitates with sulphuretted hydrogen or alkaline sulphides, though the liquids acquire a colour corresponding to the sulphide of the heavy metal which would otherwise be precipitated. The precipitation of calcium phosphate and uranyl ferrocyanide is prevented in a similar manner, while in presence of gum arabic the alkaloids are not precipitated by sodium phosphomolybdate, potassio-mercuric iodide, or tannin.

836. ASSAY OF GUM ARABIC.

Gum arabic should not contain more than about 4 per cent. of *ash*. It should be soluble almost without residue in cold water (see footnote on page 352). The solution should be free from *starch* and *dextrin*, as indicated by the negative reaction with iodine solution; but should be rendered turbid by oxalic acid, which the solution of dextrin is not. The better kinds of gum arabic do not reduce Fehling's solution when heated to boiling with it, any red precipitate being due to the presence of a reducing sugar, small quantities of which exist naturally in certain inferior varieties of gum, though any considerable quantity has probably been introduced as an impurity in an admixture of *dextrin*.

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[1] The treatment of the gums with nitric acid was conducted in the following manner :—2 grammes weight of the powdered sample was digested at 60° C., with 5 c.c. of nitric acid of 1·2 specific gravity, until the whole became a solid mass saturated with the liquid. Another 5 c.c. of nitric acid was then added and the liquid filtered. The residue of mucic acid was washed thoroughly, dried at 100°, and weighed. The filtrate and washings were evaporated together and again treated with nitric acid, when a further quantity of mucic acid was obtained, while a third treatment generally yielded only a trace in addition.

837. According to Z. Roussin (*Jour. de Pharmacie*, [4] vii. 251), *gum arabic* and *dextrin* may be distinguished and separated by means of ferric chloride, which precipitates the former only. The solution is concentrated to a syrup, mixed with ten times its volume of rectified spirit, and the resultant precipitate washed with rectified spirit and dried. 1 gramme of the dry residue is then dissolved in 10 c.c. of water, the solution mixed with 30 c.c. of proof spirit, 4 drops of ferric chloride solution (containing 26 per cent. of the anhydrous chloride) added, followed by a few decigrammes of powdered chalk; and after stirring briskly and leaving the liquid at rest for a few minutes it is filtered. The precipitate is washed with proof spirit, and the dextrin is precipitated from the filtrate by adding very strong alcohol. After twenty-four hours the spirituous liquid is decanted, the dextrin dissolved in a small quantity of water, the resultant solution evaporated at 100°, and the residue weighed. The precipitate containing the gum must be dissolved in dilute hydrochloric acid, the arabin precipitated by adding absolute or very strong alcohol, and after washing with spirit is dissolved in water, the solution evaporated, and the residue weighed. The precipitation of gum arabic from a dilute alcoholic liquid by ferric chloride and chalk is so complete that nothing but calcium chloride can be found in the filtrate, while the precipitate similarly produced in a solution of dextrin is perfectly free from the latter body. By the formation of a cloud on adding ferric chloride alone, the presence of gum arabic is sufficiently demonstrated, while the clouding of the filtrate from the iron-chalk precipitate on addition of alcohol proves the presence of dextrin.

Another test by which gum arabic may be distinguished from dextrin is given on page 349. A large proportion of dextrin would be indicated by the dextro-rotatory action of the solution, but the variation in the optical activity of both natural gum arabic and commercial dextrin would prevent the quantitative application of the test.

For the separation of gum arabic from *sugar*, Andouard dilutes 10 grammes of the syrup with 100 c.c. of spirit of ·800 specific gravity, adds 20 drops of acetic acid, and stirs vigorously. After three hours the liquid is poured on a double filter, when the gum forms a cake which readily drains. This is dissolved in a little water, and the precipitation repeated, the precipitate washed with alcohol, dried at 100° and weighed. It is then exposed to the atmosphere for twenty-four hours, when it will have taken up its normal amount of moisture.

838. The inferior kinds of gum are largely employed as thickening agents in calico-printing. Good gum neither tarnishes nor alters delicate colours, and does not weaken the mordants. The action of gums on delicate colours may be ascertained by printing a solution of the sample mixed with cochineal-pink or fuchsine upon pure wool; the fabric is then steamed and washed, when, if the gum be pure, there will be no trace of yellowness apparent. Too great an acidity of the gum gives it a solvent action on mordants, and hence renders it unsuitable for use.

839. The relative viscosity of samples of gum is an important character in judging of their quality. This may be tested by making solutions of 10 grammes of each sample in a little warm water, diluting the liquids to 100 c.c., and ascertaining the rate at which the solutions flow from a glass tube drawn out to a fine orifice. A recently prepared solution of gum of the best quality should be used as a standard.

840. Gum Tragacanth.

Gum tragacanth is the gummy exudation from ***Astragalus gummifer*** and other allied species. It occurs in flattened, tear-like masses, strings, or curved bands, which are usually marked with ridges or other indications of lamination.

841. According to Giraud, gum tragacanth usually contains about 60 per cent. of a pectinous body which yields pectic acid by boiling with water containing 1 per cent. of hydrochloric acid; from 8 to 10 per cent. of soluble gum, probably arabin; 5 to 6 per cent. of starch and cellulose; 3 per cent. of ash; 20 per cent. of water; and traces of nitrogenous bodies. The ash is chiefly calcium carbonate.

The characteristic pectinous constituent of gum tragacanth is known as tragacanthin, adracanthin, or bassorin, and is stated to have the composition $C_{12}H_{20}O_{10}$.

842. Tragacanth is usually white or yellowish (having sometimes been bleached by chlorine), but the inferior varieties have a brownish colour. It is hard, tough, and difficult to powder. Tragacanth is odourless and tasteless, and insoluble in alcohol or ether. With 50 parts of water it swells up and forms a thick jelly-like mucilage, without actually dissolving. When diffused through a much larger quantity of water it forms a ropy liquid which may be passed through a filter, leaving an insoluble residue which is coloured blue by iodine from the presence of starch. Mucilage of tragacanth is coloured yellow by caustic soda, and a solution of the gum yields clear mixtures with borax, alkaline silicates, and ferric chloride, but is precipitated by alcohol. It becomes thick on adding neutral or basic lead acetate, and on heating the mixture a precipitate is formed.

843. Before being used for calico-printing, gum tragacanth is swelled by soaking in cold water for twenty-four hours, and afterwards boiled with water for six hours, when a thick homogeneous solution results, which, however, has but little cohesive power. The comparative viscosity of the liquid can be ascertained as in the case of gum arabic (par. 839).

844. PROXIMATE ANALYSIS OF PLANTS.

The quantitative separation, and even the qualitative detection, of the various constituents of plants is often attended with great difficulty. Owing to the immense variety of bodies met with in the vegetable kingdom, it is impossible to prescribe any detailed method which shall be suitable for use in all cases. It is however, possible to devise a scheme of general proximate analysis which will be of great assistance in the examination of plant products. This has been done in a very able manner by H. B. Parsons (*Pharm. Jour.*, [3] x. 793), and it is from the methods described by him, as practised in the laboratory of Professor A. B. Prescott, that the following tables of analysis have been drawn up. It must be distinctly understood that the scheme is intended to facilitate the systematic analysis of vegetable substances, and that bodies of certain kinds having by its aid been proved to be present should be isolated or determined by the special methods to be found under the heads of cellulose, starch, dextrin, sugars, cinchona barks, tannin, &c.

Moisture is determined by drying a known weight of the finely-divided substance at 100 to 120° C. The loss of weight represents water, and sometimes a little volatile oil. In some cases it is necessary to dry the substance at a lower temperature, or to employ a current of dry coal-gas or carbon dioxide.

Mineral Matter is determined in the manner and with the precautions described in par. 95 *et seq.*

Total Nitrogen is determined by igniting the substance with soda-lime, and estimating the ammonia formed. The amount of nitrogen found may, if required, be calculated to its equivalent in albuminoids by multiplying it by the factor 6·33.

It must not be assumed, however, that all the nitrogen present exists as albuminoids, the contrary being commonly the case. An outline of the method of estimating the nitrogen existing in various forms is given in the footnote on page 366, but if alkaloids be present they must be isolated by separate means.

845. Action of Solvents.—The substance is then submitted to a systematic treatment with solvents and reagents in the manner prescribed in the following tables :—

<table>
<tr><td colspan="7">Treat 5 grammes of the finely-divided substance with benzene wholly distilling below 86° C., or, failing this, with chloroform. The treatment should be continued for six hours, and be conducted in a Soxhlet's extractor (par. 82), or other suitable apparatus for re-percolation.</td></tr>
<tr><td rowspan="6">A. <i>Solution</i> may contain alkaloids, glucosides, free organic acids, chlorophyll, certain resins, fixed oils, fats and waxes, camphors, volatile oils, but no mineral matter.</td><td colspan="6"><i>Residue.</i>—Dry at 100° C., weigh and treat with redistilled methylated spirit of ·848 sp. gravity for twelve hours in a Soxhlet's tube.</td></tr>
<tr><td rowspan="5">B. <i>Solution</i> may contain mineral matters, tannin, organic acids, alkaloids, glucosides, certain extractive and colouring matters, resins, and sugars.</td><td colspan="5"><i>Residue.</i>—Dry at 100° C., weigh and treat with a known measure of cold water. Macerate, with frequent agitation, for eight or ten hours. Then filter through fine washed linen, or paper if possible.</td></tr>
<tr><td rowspan="4">C. <i>Solution</i> may contain soluble albuminoids, gum; and, in the analysis of fruits and fleshy roots, pectin bodies, salts of organic acids, dextrinoid bodies, and colouring matters.</td><td colspan="4"><i>Residue.</i>—Wash with alcohol, dry at 100°, and weigh. Then treat with 500 c.c. of water and 5 c.c. of concentrated sulphuric acid, and heat till a drop of the liquid gives no colour with iodine,</td></tr>
<tr><td rowspan="3">D. <i>Solution</i> may contain dextrin and maltose from conversion of starch; also albuminoids, and occasionally organic acids, either as salts or free.</td><td colspan="3"><i>Residue.</i>—Wash thoroughly, dry at 110° C. and weigh. Boil for two hours with 500 c.c. of a 2 per cent. of caustic soda. Filter through washed linen.</td></tr>
<tr><td rowspan="2">E. <i>Solution</i> may contain albuminous matters, pectous matters, cutose, humus, and products of decomposition.</td><td colspan="2"><i>Residue.</i>—Wash thoroughly in succession with hot water, alcohol and ether. Dry at 110°C. and weigh. Treat with dilute bromine water and ammonia, as directed on page 320.</td></tr>
<tr><td>F. <i>Solution.</i>—Lignin and colouring matter.</td><td><i>Residue.</i>—Weigh as cellulose.</td></tr>
</table>

A. Solution in Benzene or Chloroform.—Evaporate carefully to dryness, and weigh the residue. Then treat with water; again evaporate to dryness at 100°, heat to 110°, and weigh again.

<table>
<tr><td rowspan="4"><i>Volatilised.</i> — Volatile oils, camphors (partially), volatile alkaloids. The last may be detected by the alkaline reaction of the aqueous liquid, and their loss avoided by adding a drop of hydrochloric acid before evaporation.</td><td colspan="4"><i>Residue.</i>—Treat with a moderate quantity of warm water, and when cold filter through fine paper by Bunsen pump.</td></tr>
<tr><td rowspan="3"><i>Solution.</i>—Divide into two equal portions <i>a.</i> and <i>b.</i>—
<i>a.</i> Evaporate to dryness, and weigh total extract. Ignite, and weigh ash.
<i>b.</i> Test portions for alkaloids and glucosides by special reagents; and for organic acids by solutions of barium, calcium, iron, lead, and silver.</td><td colspan="3"><i>Residue.</i>—Remove from the filter and vessels used by benzene or chloroform, and agitate solution with warm, very dilute hydrochloric acid, and separate by means of a tapped funnel. (See figure on page 31.)</td></tr>
<tr><td rowspan="2"><i>Acid Solution.</i>—Test for alkaloids and glucosides.</td><td colspan="2"><i>Benzene Solution.</i>—Evaporate to dryness, and treat residue several times with spirit of ·848 sp. gr. Filter through paper.</td></tr>
<tr><td><i>Solution</i> may contain camphors, resins, chlorophyll, certain fixed oils (<i>e.g.</i> castor oil). Camphors are recognisable by the smell; Chlorophyll by its absorption - spectrum.</td><td><i>Residue</i> consists of fixed oils, fats, wax, and, very rarely, resin.</td></tr>
</table>

B. SOLUTION IN ALCOHOL OF ·848 SPECIFIC GRAVITY.—Concentrate to a small bulk, and remove, dry, and weigh any crystals or powder which may separate from the cooled liquid. Dilute the clear liquid to 200 c.c. by spirit of ·848 specific gravity, and divide into several aliquot parts (20, 20, and 160 c.c.).

<table>
<tr>
<td rowspan="4">20 c.c.—Evaporate to dryness, and weigh total extract. Ignite and weigh again to determine ash and total organic extract.</td>
<td rowspan="4">20 c.c.—Evaporate nearly to dryness; add water, filter, and evaporate filtrate to dryness. Residue is soluble extract, and on ignition leaves the soluble ash.</td>
<td colspan="6">160 c.c.—If much sugar or tannin be present (recognisable by the taste) employ process <i>a</i>; if but little of either of these be present use process <i>b</i>.</td>
</tr>
<tr>
<td colspan="2">(<i>a</i>) Evaporate nearly to dryness, add water, filter, and make up filtrate to 160 c.c.</td>
<td colspan="4">(<i>b</i>) Evaporate carefully to dryness, pulverise and treat residue with several considerable portions of absolute alcohol (specific gravity ·7938). Filter.</td>
</tr>
<tr>
<td rowspan="2"><i>Residue</i> may contain resins; colouring matters; albuminoids, especially from seeds; alkaloids, and glucosides.</td>
<td rowspan="2"><i>Solution.</i>—Divide into eight portions of 20 c.c. each.
1. Precipitate tannin with ammoniacal zinc acetate. The loss of weight by carefully igniting the weighed precipitate dried at 120° represents tannin.
2. Add neutral lead acetate. Loss of weight on ignition represents tannic, gallic, and other organic acids, colouring and extractive matters, and, rarely, albuminoids.
3 and 4. Precipitate by basic lead acetate, and treat as in 2. After separating lead, treat one half of filtrate with Fehling's solution to estimate glucose; invert other portions and determine glucose; the difference gives glucose formed from glucosides and sucrose.
5 and 6. Treat with basic lead acetate and filter. Decompose both precipitate and filtrate with H_2S, testing the first for organic acids, and latter for alkaloids and glucosides.
7 and 8. Use in case of accident to other portions.</td>
<td colspan="2"><i>Solution.</i>—Evaporate nearly to dryness, and add water.</td>
<td colspan="2"><i>Residue.</i>—Treat with water.</td>
</tr>
<tr>
<td><i>Solution.</i>—Add basic acetate of lead. Loss of weight on igniting <i>precipitate</i> represents tannin, organic acids, and some extractives. <i>Filtrate</i> may contain alkaloids, glucosides, extractive and colouring matters.</td>
<td><i>Residue</i> may contain—
1. Alkaloids, glucosides (rarely), and extractives soluble in dilute HCl.
2. Matters insoluble in dilute HCl.
3. Acid resins and colours soluble in dilute ammonia.
4. Neutral resins, colours, and nitrogenous matters insoluble in dilute ammonia.</td>
<td><i>Solution.</i>—Add basic lead acetate. Loss of weight on igniting <i>precipitate</i> represents colours, extractives, organic acids, albuminoids (rarely). <i>Filtrate</i>; remove lead, and determine glucose by Fehling's solution, and glucosides and sucrose by increased reduction after inversion.</td>
<td><i>Residue.</i>—Treat with dilute HCl.
1. Dissolved; some alkaloids and glucosides.
2. Insoluble; some resins, and colouring and extractive matters. Dissolve in alcohol; evaporate to dryness, and weigh.</td>
</tr>
</table>

C. Solution in Cold Water.—Make up liquid to known volume and divide into aliquot portions.

1. Determine *total solid matter* by evaporating and drying residue at 110° C. Determine *ash* by ignition.
2. Add solution of iodine. A blue colour indicates *soluble starch*; a reddish-brown colour, *erythro-dextrin*.
3. Add ammonium oxalate. A white precipitate indicates calcium, probably as calcium *arabinate*.
4. Evaporate known volume, ignite residue with soda-lime, and multiply nitrogen found by 6·33 to estimate *albumin*.
5. Add dilute hydrochloric acid. A gelatinous precipitate consists of *pectin* or *pectic acid*; if the liquid be filtered and treated with four times its measure of alcohol, a further precipitate may consist of *arabin* or *dextrin*.

D. Solution in Dilute Acid.—Boil with excess of barium carbonate, exactly neutralise last traces of acid by cautious addition of baryta-water, filter, concentrate, and bring volume to exactly 50 c.c. Then ascertain specific gravity, and divide excess above 1000 by 8. The figure thus obtained is the weight of starch in the 5 grammes of substance taken. If the density indicates but a small proportion of starch, treat half the solution with 1 c.c. of concentrated sulphuric acid, and heat the liquid to 100° for three or four hours (par. 508); then neutralise, and estimate glucose by Fehling's solution. Amount found, multiplied by 0·9, gives *starch*. Test portion of original neutralised solution by adding tannin. A white or buff precipitate indicates *albuminoids*.

E. Solution in Dilute Alkali.—Add slight excess of hydrochloric acid. A precipitate may contain *pectic acid* and other bodies, *colouring matters*, &c. Further precipitation usually occurs on adding alcohol.

846. COMPOSITION OF CEREALS, &c.

A very large number of analyses of wheat and other grains have been published by different chemists, but unfortunately many of them are of doubtful value, owing to the defective methods of analysis employed.

The following is the average composition of the cereal grains, according to Chas. Graham:—

	Old Wheat.	Barley.	Oats.	Rye.	Maize.	Rice.
Water, . .	11·1	12·0	14·2	14·3	11·5	10·8
Starch, . .	62·3	52·7	56·1	54·9	54·8	78·8
Fat, . . .	1·2	2·6	4·6	2·0	4·7	0·1
Cellulose, . .	8·3	11·5	1·0	6·4	14·9	0·2
Gum and Sugar,	3·8	4·2	5·7	11·3	2·9	1·6
Albuminoids, .	10·9	13·2	16·0	8·8	8·9	7·2
Ash,[1] . .	1·6	2·8	2·2	1·8	1·6	0·9
Loss, &c., . .	0·8	1·0	0·2	0·5	0·7	0·4
	100·0	100·0	100·0	100·0	100·0	100·0

A. H. Church gives the following analyses by himself in illustration of the composition of representative specimens of the cereal grains and products therefrom:—

	White English Wheat.	Fine Wheat Flour.	Wheat Bran.	Scotch Oatmeal.[2]	Pearl Barley.[3]	Rye Flour.	Cleaned Rice.	Maize	Millet.	Dari.
Water, . . .	14·5	13·0	14·0	5·0	14·6	13·0	14·6	14·5	13·0	12·2
Albuminoids and other nitrogenous bodies, .	11·0	10·5	15·0	16·1	6·2	10·5	7·5	9·0	15·3	8·2
Starch, with traces of Dextrin, &c., . .	69·0	74·3	44·0	63·0	76·0	71·0	76·0	64·5	61·6	70·6
Fat, ...	1·2	0·8	4·0	10·1	1·3	1·6	0·5	5·0	5·0	4·2
Cellulose and Lignose,	2·6	0·7	17·0	3·7	0·8	2·3	0·9	5·0	3·5	3·1
Mineral matter,[1] .	1·7	0·7	6·0	2·1	1·1	1·6	0·5	2·0	1·6	1·7
	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

847. For convenience of comparison, the following analyses of

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[1] The composition of the ash of cereals is considered on page 368.

[2] 100 lbs. of oats yield about 60 of oatmeal and 26 of husks, the remainder being water and loss.

[3] The product called pearl-barley constitutes only about one-third of the whole seed.

other vegetable products are given. They are selected from among a large number published in Church's valuable work on *Food*:—

	Buck-wheat.	Peas.	Haricot Beans.	Lentils.	Earth-nuts, Shelled.
Water, ...	13·4	14·3	14·0	14·5	7·5
Albuminoids, &c., . .	15·2	22·4	23·0	24·0	24·5
Starch, &c., . . .	63·6	51·3	52·3	49·0	11·7
Fat, ...	3·4	2·5	2·3	2·6	50·0
Cellulose and Lignose, .	2·1	6·5	5·5	6·9	4·5
Mineral matter, . .	2·3	3·0	2·9	3·0	1·8
	100·0	100·0	100·0	100·0	100·0

	Potatoes.	White Turnips.	Carrots.	Beet-root, Red.	Yam.
Water, ...	75·0	92·8	89·0	82·0	79·6
Albuminoids, &c., . .	2·3	0·5	0·5	0·4	2·2
Sugar, ...	...	...	4·5	10·0	16·3
Starch, ...	15·4	...	...	...	
Dextrin, Gum, and Pectose,	2·0	4·0	0·5	3·4	
Fat, ...	0·3	0·1	0·2	0·1	0·5
Cellulose and Lignose, .	1·0	1·8	4·3	3·0	0·9
Mineral matter, . .	1·0	0·8	1·0	0·9	1·5

848. **Albuminoids of Cereals.**

Of the bodies known to chemists as albuminoids or proteids, numerous species are found in the vegetable kingdom. Although differing somewhat in composition, the percentage of nitrogen found in them by the soda-lime process does not vary very greatly from the average of 15·8. Hence it is very usual to deduce the proportion of albuminoids present by multiplying the percentage of nitrogen by 6·33 $\left(=\frac{100}{15\cdot8}\right)$, and to ignore the fact that the whole of the nitrogen of plants does not exist in the form of proteids, but may be present as true albuminoids, peptones, alkaloids, amido-acids, nitrates, &c. Hence an expression of the proportion of the total nitrogen as "albuminoids" is very misleading if the analysis is to be used to judge of the suitability of a cereal for bread-making, or as an article of diet generally, and it is desirable therefore to acquire a more complete knowledge of the nature and amount of the nitrogenised bodies present than is obtainable from a mere determination of the nitrogen, and the calculation of the amount found to its equivalent of albuminoids.[1]

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[1] A detailed description of the nitrogenous constituents of plants, and of the methods of separating them, is given in Dragendorff's *Plant-Analysis*, translated by H. G. Greenish.

849. GLUTEN.—When wheaten flour is kneaded in a stream of water, the starch is gradually washed away, and there remains a sticky cohesive mass which is very rich in nitrogen.[1] The "crude gluten" so obtained consists chiefly of a mixture of gluten-fibrin, gliadin or glutin, and mucedin, with small quantities of fat and mineral matter.

850. *Gluten-fibrin*, or *Vegetable fibrin*, is insoluble in water or alcohol. It readily undergoes decomposition in the moist state, first producing soluble albuminoid bodies and ultimately offensive products. Gluten-fibrin constitutes about 80 per cent. of the "crude gluten," and dissolves with facility in cold dilute acids (acetic, citric, tartaric, hydrochloric), and in caustic alkali. It is precipitated from its acid or alkaline solutions on neutralisation, and is thrown down by cupric acetate.

Gluten-fibrin may be obtained pure by boiling the crude gluten several times with alcohol of ·890 specific gravity, and treating the residue with weak alkali. The intermixed starch and cellulose are left insoluble, while the fibrin may be reprecipitated from the solution by adding acetic acid. The spirituous solution contains *gliadin* or *glutin*, and *mucedin*, both of which bodies are somewhat soluble in cold water and weak alcohol, especially when hot, but are insoluble in absolute alcohol. Mucedin is deposited when the hot spirituous liquid is cooled.

851. *To determine the proportion of gluten* obtainable from flour, 50 grammes of the sample should be triturated in a mortar with 30 grammes of water. The dough produced should leave the mortar without leaving a trace behind. After standing at rest for three or four hours, the mass is placed in a fine linen cloth, which is then tied up and gently kneaded with the fingers, while a fine stream of water is permitted to flow on to it. The kneading and washing are continued until the water which runs away is found to be clear, and hence free from starch. The gluten is then removed from the cloth and dried slowly at 110 to 120° C. Gluten from good flour is elastic and but little coloured: that from damaged or inferior flour adheres to the cloth, is with difficulty united into a single mass, and has less consistency and a higher colour than the product from good flour.[2]

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[1] According to Weyl and Bischoff, if the flour be treated with a 15 per cent. solution of chloride of sodium, the myosin is dissolved out, and the remaining flour is found to have lost the property of forming a gluten-mass.

[2] When the gluten is not to be subsequently examined in the aleurometer, it is preferable to operate on 10 grammes of the flour, instead of on 50 as directed in the text.

The following alternative method of determining the gluten of flour, is

M. Balland has pointed out (*Compt. rend.*, xcvii. 496) that the proportion of gluten obtained from the same flour varies with the mode of operation and amount of washing. A more hydrated gluten is yielded by flour from soft or old wheat than hard, and by fresh paste than by paste which has stood several hours before washing. In order to avoid these sources of error, it is recommended that 50 grammes of the flour should be mixed with 25 grammes of water, and the paste allowed to stand for twenty-five minutes. It is then divided into two equal portions, one of which is washed immediately, while the other is allowed to stand an hour. As soon as the wash-water is clear, the glutens are tightly pressed and weighed, after which they are washed for another five minutes and again weighed. Four numbers are thus obtained, and the mean of these is taken as the true amount of gluten present.

852. It is sometimes of advantage to ascertain the physical characters of the crude gluten obtained as above. This is facilitated by the use of the *aleurometer*, an instrument devised by Balland. It consists of a copper or brass cylinder, furnished with a piston. From 30 to 50 grammes of flour should be washed in the manner already described. 7 grammes' weight of freshly separated gluten is placed in the cylinder, and the piston pushed down till it registers 25°. The cylinder is then heated to 150° C. for ten minutes, when the gluten will be found to have expanded and forced up the piston to an extent dependent on its quality. Good flour yields a gluten which will swell to four times its original volume. With damaged flour the gluten does not swell much, but becomes viscous or nearly fluid, adheres to the cylinder, and sometimes exhales a disagreeable odour, whereas good gluten has merely the odour of hot bread. If the gluten does not indicate at least 25° on the aleurometer it may be considered unfit for bread-making.[1]

853. L. Reed (*Chem. News*, xlviii. 63) has proposed to make a rough assay of flour for gluten by observing the intensity of the

recommended by Wanklyn and Cooper :—10 grammes' weight of the sample is mixed on a porcelain plate with 4 c.c. of water, so as to obtain a homogeneous dough. This is placed in a conical measure or other suitable vessel, 50 c.c. of water added, and the dough manipulated with a spatula so as to expel the starch-granules. The water is decanted off, a fresh quantity added, and the kneading repeated till no more starch is extracted from the gluten. The mass is then removed and kneaded in a little ether, after which it is spread out in a thin layer on a platinum dish and dried in the water-oven till the weight is constant. The crude gluten contains ash equal to about ·3 per cent. on the flour, and fat equivalent to 1·00 of the flour. These may, of course, be directly determined in the crude gluten, if desired.

[1] Balland's aleurometer is obtainable from Clarke and Denham, 24 Mark Lane, E.C.

yellow coloration produced by nitric acid. Operating in the manner prescribed by him, and also with certain modifications, the writer has not found the difference in the intensity of the yellow sufficiently marked to be of much service in practice.

854. VEGETABLE ALBUMIN, and LEGUMIN or vegetable casein are soluble in cold water, and hence pass into solution when the flour is kneaded in the manner above described. The albumin may be coagulated by boiling the liquid, and the legumin precipitated from the filtrate by adding acetic acid.

855. CEREALIN is a soluble nitrogenised ferment occurring especially in the husk or bran of wheat and other cereals. It has a powerful fermentative action on starch, rapidly converting it into dextrin and other soluble bodies. Cerealin is precipitated by alcohol and acids.

Other soluble nitrogenous bodies besides cerealin have a marked power of converting starch, and seeds of meals containing them in large proportion are unsuited for making bread. Thus, if barley meal be kneaded with water in the manner already described, but very little crude gluten will be obtained, although barley is richer than wheat in total nitrogen. Barley flour, consequently, if made into bread yields a heavy, doughy mass. Rye flour, which contains a large proportion of total nitrogen, leaves little or no crude gluten when kneaded, and hence does not yield the tough, elastic dough so characteristic of wheat flour. The same is true of oat flour and maize flour.

The presence of cerealin in bran renders whole meal unsuitable for making bread by fermentation with yeast, though "aërated bread" can be prepared from it. The cerealin acts like malt-extract, causing a rapid conversion of the starch into dextrin and sugar, and hence all admixture of the flour with bran should be carefully avoided.[1]

856. Wanklyn has applied his well-known albuminoid ammonia process to the determination of the nitrogenised principles of flour (*Phil. Mag.*, May, 1877). For the estimation of the total albuminoids 1 gramme of the sample is dissolved in 20 c.c. of a 5 per cent. solution of caustic potash, and the liquid diluted to 1 litre. 10 or 20 c.c. measure of this solution is next distilled with 50 c.c. of the alkaline solution of permanganate and 500 of

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[1] The use of whole meal is often advocated on account of the high proportion of nitrogenous matter and ash-constituents present in it, but the admixture of oatmeal with wheat flour might be advocated on precisely similar grounds. The indigestibility of the bran wholly neutralises any advantage supposed to be derivable from its superior nutritive value. See also the experiments of Rubner (*Jour. Chem. Soc.*, xlvi. 622).

ammonia-free water, the distillate being nesslerised in the usual way. The soluble albuminoids are determined in a similar manner, except that 10 grammes of the sample are taken and mixed up thoroughly with cold water, the mixture diluted to 100 c.c., filtered, 10 c.c. of the filtrate diluted to 100 c.c., and 10 c.c. of the dilute liquid (= ·1 gramme of flour) distilled with permanganate. *Assuming* that the ammonia corresponds to ten times its weight of albuminoids, sound flour yields about 1 per cent. of albumin, &c., to cold water, while the total albuminoids range from 9·2 to 11·7 per cent. Pea flour gave 23; rice, 6·2; maize, 10·3; oats, 10·0; barley, 11·0; malt, 5·0; and arrowroot, 0·8 per cent. of total albuminoids, calculated at ten times the ammonia yielded on distillation with alkaline permanganate.

857. C. Graham has suggested a simple method of making rough comparative estimates of the soluble albuminoids of different samples, which, with certain modifications, is as follows:—10 grammes' weight of the flour is treated with 40 c.c. of cold water, and the mixture allowed to stand for exactly one hour. The liquid is then passed through a dry filter, the first portions being rejected. 20 c.c. measure of the filtrate (= 5 grammes of flour) is then treated with an equal measure of methylated spirit, when a precipitate of soluble albuminoids will be produced, the amount of which will depend on the quality of the flour, the best specimens giving the smallest precipitate. A more accurate estimation of the soluble albuminoids may be made by filtering the liquid, evaporating 20 c.c. of the filtrate to dryness at 100° C., and weighing the residue of sugar, &c. The weight thus obtained is subtracted from that found by evaporating 10 c.c. of the original aqueous solution of the flour, when the difference will be the weight of soluble albuminoids precipitated by the methylated spirit. It is necessary to adhere strictly to one hour, or other constant time, for the digestion of the flour with water, as higher results are obtained if the treatment be prolonged. Operating in the foregoing manner, J. W. Downs informs the writer that the matter dissolved by cold water from flour ranges from 6·7 in samples of the lowest quality to 3·5 per cent. in the highest quality of flour, the average being about 5 or 5½ per cent.

858. The albuminoids of wheat and other cereals may therefore be classed broadly as soluble and insoluble, the latter being of service in the formation of a firm elastic gluten, and the former being rather detrimental than otherwise in the production of bread.[1] It has been pointed out by Graham that a constant ratio

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[1] Schulze and Barbieri (*Jour. Chem. Soc.*, xl. 312) in discussing the insufficiency of the ordinary methods of discriminating between the different

exists between the proportion of soluble albuminoids and the dextrin and sugar found on analysing the flour, and the longer the flour is digested in cold water the greater the proportion of soluble albuminoids, and hence of dextrin and sugar, becomes.

859. **Mineral Constituents of Cereals.**

The following table shows the percentage of ash or mineral matter contained in nine different fractions obtained by grinding wheat containing 1·634 per cent. of mineral matter. The numbers given are the average results of the examination of twenty-eight samples, the experiments extending to the products of three separate years. It appears, therefore, that of the total ash of the grain, amounting to 1·634 per cent. of its weight, ·483 occurs in the first three products ("fine flour"), and that in the first five taken together the ash amounts to ·723. These three products constitute upwards of 80 per cent. of the weight of the original grain, and their mixture fairly represents the composition of good seconds flour, with an ash of ·86 per cent. Even with the addition of products 6 and 7 of the following table, the ash of the flour only amounts to about 0·9 per cent. Hence it may safely be assumed that no sample of flour in which bran is not very notably present ever yields a higher ash that 1·00 per cent. The

forms of nitrogenised bodies existing in plants, very properly recommend that the true soluble albuminoids should be distinguished from the peptones, and these again from the amido-compounds. For the qualitative detection of albuminoids the formation of a precipitate on adding acetic acid and potassium ferrocyanide will suffice. For the precipitation of the *albuminoids*, various reagents, such as tannin, ferric acetate, cupric acetate, plumbic hydroxide, &c., should be employed on separate portions of the solution, the precipitate containing least nitrogen being considered that which represents the true albuminoids. The *peptones*, which in nutritive value are equal, or nearly so, to the albuminoids, may be precipitated from the filtrate by means of phosphotungstic acid. The *amido-compounds*, which remain in the solution from which the proteids and peptones have been precipitated, are typified by asparagine and glutamine, and may, if desired, be determined by boiling the solution with an acid, and then estimating the ammonia from the amount of gas liberated by sodium hypobromite. Leucine, caffeine, creatine, and other bases also evolve nitrogen when thus treated. Hence a preferable method is to decompose the acid amides into amido-acids by boiling with dilute acid, remove the ammoniacal salts, and treat with potassium nitrite and dilute sulphuric acid, when the nitrogen evolved is measured. For the estimation of the ammonia originally present in the plant, treatment with milk of lime in the cold, under reduced pressure, is recommended.

In analysing plant-products it is very important that in the extraction of the nitrogenous constituents they should undergo little or no change in composition. Schulze and Barbieri consider this may be best effected by extracting first with cold and then with hot water, or else with dilute alcohol.

ash of fine flour is more often below 0·70 per cent. than in excess of that number, and of late years the writer has often found it as low as 0·50 per cent. :—

	Yield from 100 Parts of Meal.	Percentage of Ash in Products.	Distribution of Total Ash.
1. Fine Flour, . . .	41·1	·69	·284
2. ,, ,, ...	18·6	·71	·132
3. ,, ,, ...	9·2	·73	·067
Products 1, 2, and 3 together	70·2[1]	·71	·483
4. "Tails," . . .	5·3	1·03	·054
5. "Fine Sharps" or "Middlings,"	8·8	2·12	·186
Products 1 to 5 together, .	84.3	·86	·723
6. "Coarse Sharps," . .	3·4	4·18	·142
7. "Fine Pollard," . .	2·4	5·65	·136
8. "Coarse Pollard," . .	6·5	6·47	·420
9. "Long Bran," . .	3·0	7·11	·213
			1·634

860. The *amount* of ash of cereals is not influenced in any definite manner by the nature of the soil, and the same is true of the *composition* of the ash, the predominance of any particular constituent in the soil by no means leading to an excessive proportion of the same substance in the ash of the plant. (See a laborious series of analyses of the ashes of wheat-grain and straw, by Lawes and Gilbert, *Jour. Chem. Soc.*, xlv. 305 to 407).

The difference in the proportion of ash yielded by the grain, chaff, and straw of cereals is strictly confined to the silica; if this be deducted, the remainders present no perceptible difference.

The percentage of ash yielded by barley and oats is somewhat higher than that from wheat, while rye and maize yield about the same as wheat, and rice far less.[2]

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[1] There seems to be an error here, but a careful inspection of the original tables has failed to detect its nature. With the exception of the line commencing "Products 1 to 5 together," the numbers in which have been calculated by the writer, the figures are taken from the original paper by Lawes and Gilbert (*Jour. Chem. Soc.*, x. 27).

[2] The composition of the ash of the whole grain of wheat and other cereals has been studied by Lawes and Gilbert, Chevalier, Way and Ogston, &c. The following are the general practical conclusions deducible from the numerous analyses recorded :—

The proportion of potash is very variable, but useless as a means of distinguishing the ash of different grains. The lime ranges from 1 to 10 per cent. Baryta has been found in Egyptian wheat. The magnesia varies

861. Adulterations of Flour and Bread.

The adulterations to which bread and wheaten flour are liable are of two kinds:—admixture with the flour or meal of other cereals, and addition of mineral substances. The first kind of sophistication can, as a rule, only be ascertained by a patient examination under the microscope (see page 375), and there are cases in which even this plan fails to be of service. Mineral adulterants may occasionally be used to increase the weight or bulk of the article, but such employment of them is now practically obsolete, and their use is limited to increasing the whiteness and apparent quality of the bread made from the flour. *Alum* is the addition usually made for this purpose, but *plaster of Paris* and similar materials are occasionally employed.

862. Mineral Additions to Flour and Bread.

In the case of flour, a determination of the ash affords a sufficiently accurate means of detecting and determining mineral adulterants, with the exception of alum, which is usually employed in too small a quantity sensibly to affect the percentage obtained. With wheaten flour, any higher ash than 0·7 per cent. should be regarded with great suspicion, but in the case of oatmeal 2 per cent. or somewhat more is a normal proportion.

In consequence of the ease with which the mineral adulterants of flour can be separated from the sample, it is rarely necessary to

much, but in wheat-ash is pretty constant, fifty-three samples analysed by various chemists showing a range from 9·1 to 14·3, with a mean amount of 12·11 of MgO in 100 of ash. The ferric oxide in wheat-ash was found by Way and Ogston to range from 0·1 to 3·3 per cent., but Lawes and Gilbert (*Jour. Chem. Soc.*, xlv. 305) never found a proportion sensibly in excess of 1 per cent., which number doubtless includes any trace of alumina which may have been present. Meunier finds from 0·69 to 1·75 per cent. of ferric oxide in wheat-ash, with an average of 1·11 per cent. Alumina is present only in minute traces, the proportion in genuine wheat-flour ash rarely exceeding 1 per cent., and even this is probably due to adherent dirt. The silica in the ash of wheat, rye, maize, and rice is generally very low, rarely reaching 5, and being usually less than 2 per cent. of the total. In barley-ash, on the other hand, Chevalier found from 17·3 to 32·7, the usual amount being about 24 per cent., while the ash of oats contains from 40 to 50 per cent. of silica. Except in the larger proportion of silica the ashes of barley and oats resemble wheat-ash in every essential respect. The phosphoric acid (P_2O_5) in wheat-ash varies from 40 to 55, with a very constant average of 49 to 50 per cent., which is 10 per cent. more than is present in the ash of barley, and 20 per cent. in excess of the usual proportion in oats. On the other hand, the ash of maize or rye contains 40 to 50 per cent. of P_2O_5, and in rice-ash the proportion is still larger. In estimating phosphoric acid in cereals it is necessary to fuse the ash with sodium carbonate, to convert the pyrophosphates into orthophosphates.

determine any of the constituents of the ash, but in the case of bread this procedure will be found important.

863. The best means of *separating* any mineral adulterants from flour or oatmeal is to place 100 grammes (or 4 ounces) of the sample in a dry cylindrical separator (fig. 11), furnished with a tap below and a stopper above. About 200 to 250 c.c. of methylated chloroform should then be added, and the whole thoroughly shaken together and then left at rest for some hours, or until the flour has risen to the surface of the chloroform. Any mineral adulterant present will then be found to have sunk to the bottom of the chloroform, and on running off a little of the liquid through the tap will pass with it. The small quantity of chloroform thus obtained may be diluted with more chloroform in a smaller separator, and again allowed to settle. The second deposit may still contain a little bran and other organic matters, but will consist chiefly of sand from the mill-stones, dirt, and any alum, plaster of Paris, or other mineral powder heavier than chloroform that happened to be in the sample. The deposit is tapped off, and the bulk of the chloroform having been got rid of by decantation or filtration, the last traces are driven off by a current of air assisted by very gentle heat, and the residue is weighed. It is next examined under a microscope, using a low power, with the view of detecting particles of *alum* or other crystalline matter. The residue is then dissolved in a little cold water, and the liquid filtered. The residue should be ignited and weighed. It will contain the dirt and mill-stone dust of the sample, mixed with any *plaster of Paris*, *chalk*, *barium sulphate*, or other mineral adulterant insoluble, or nearly insoluble, in water. If the amount found does not exceed 0·1 per cent. of the weight of flour it need not be further examined. The portion of the chloroform-deposit soluble in cold water will contain any *alum* present in the original flour. On evaporating the aqueous liquid to dryness the alum will be left, and may be recognised by its astringent taste, reaction with logwood, and the form of any crystals which may have been produced. Its amount may be accurately ascertained by determining the sulphates or aluminium, and calculating to the equivalent in alum.

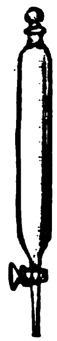

Fig. 11.

In the case of bread, oatcake, and other products obtained by adding water to the ground cereal, the chloroform treatment is not available for the detection of mineral adulterants.[1] In this case it is necessary to estimate the ash, and not unfrequently to make a partial analysis of it.

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[1] The chloroform test has been applied by L. Siebold to the examination of certain drugs (*Analyst*, iv. 19), of which the following, when free from

864. The mineral additions liable to be made to bread and other preparations of the cereals include the following substances:—1. Common salt. 2. The ingredients of common salt, added in the form of hydrochloric acid and sodium bicarbonate. 3. Baking powders; of very variable character, but usually containing sodium bicarbonate and tartaric acid. Acid phosphate of calcium and certain compounds of aluminium are also contained in some baking powders. 4. Lime water. 5. Magnesium carbonate. 6. Alum and equivalent preparations containing aluminium. 7. Plaster of Paris. 8. Whiting. 9. Barium sulphate.

Of this somewhat formidable list, the compounds of aluminium and the sulphates of barium and calcium are the only additions to which grave exception can be taken when only small proportions are used, though the earthy carbonates must be regarded as objectionable to some extent.

865. *Alum*, or an equivalent preparation containing aluminium, is by far the most common mineral adulterant of bread, though its use has greatly decreased of late years. Its action in increasing the whiteness and apparent quality of inferior flour is unquestionable, though the cause of its influence has not been clearly ascertained. Whether there be sufficient foundation for the statements made respecting the injurious effects of alumed bread on the system is still an open question. The proportion of alum which may be present is a factor too often overlooked.[1]

Alum can be detected in bread or flour, even when present in

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mineral additions, were found to float entirely on the surface of the liquid; gum arabic, gum tragacanth, starches, myrrh, Barbadoes aloes, jalap, saffron, cinchonas, nux vomica, mustard, white pepper, capsicum, and guarana. The following drugs only partially float on the chloroform, the last two chiefly subsiding:—gamboge, scammony, soccotrine aloes, opium, liquorice-root, ginger, colocynth, cousso, ipecacuanha, cinnamon, and cardamoms.

[1] Dr James Bell, in his useful little book on *Foods* (part ii. page 138), writes:—"Whichever view be held, there can be little difference of opinion that the safest course to adopt is to regard the addition of alum as unnecessary in the process of baking, and that when it is found its presence should be dealt with as a clear case of adulteration. Alum is not added to bread to improve its fitness as food, but simply to lead the public to infer from its whiteness and general appearance that the bread has been made from a better description of flour than has really been the case."

As the best descriptions of flour, and those that do not require the adventitious aid of alum, are those which contain most gluten, it is evident that the use of alum gives a false idea of the nutritive value of the flour.

very small proportion, by the careful application of the logwood-test, which was first proposed by Hadow, but modified and greatly improved by Horsley, and further worked out by J. Carter Bell. To prepare the tincture of logwood required for the test, 5 grammes of freshly-cut logwood chips or shavings should be digested in a closed bottle with 100 c.c. of methylated spirit.

866. To test for alum in flour, 10 grammes of the sample should be mixed in a glass basin or wide beaker with 10 c.c. of water. 1 c.c. of the logwood tincture and an equal measure of a saturated aqueous solution of ammonium carbonate are then added, and the whole mixed together thoroughly. If the flour be pure, a pinkish colour, which gradually fades to a dirty brown, is obtained; whereas, if alum be present, the pink is changed to lavender or actual blue. As a precaution, it is desirable to set the mixture aside for a few hours, or, heat the paste in the water-oven for an hour or two, and note whether the blue colour remains.

867. To test for alum in bread, 5 c.c. of the logwood tincture should be diluted with 90 of water and 5 c.c. of saturated carbonate of ammonium solution added. Then, without delay, the mixture is poured over about 10 grammes of the bread contained in a glass dish or clock-glass. After about five minutes, the liquid is drained away and the bread slightly washed and dried at 100° C. If alum be present, the bread will assume a lavender or dark blue colour, which becomes still more marked on drying. With pure bread, the reddish colour first obtained fades to a buff or light brown. With care and a little practice the test is very satisfactory, and is so delicate that even 7 grains of alum to the 4 lb. loaf can be detected. With moderate proportions of alum, the depth of colour produced will roughly indicate the amount of the adulterant present.[1]

868. A. Wynter Blyth modifies the logwood test by treating the flour or bread with a moderate quantity of cold water, and immersing

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[1] In employing the logwood test for alum, it is very important that the tincture of logwood should be freshly prepared, and that the test should be made immediately after mixing the logwood tincture with the solution of ammonium carbonate. Inattention to these essential points has caused the failure of several chemists to obtain the blue coloration with specimens undoubtedly containing alum. The subsequent drying also should never be neglected. With proper care, the test is exceedingly delicate, 0·02 per cent. of alum causing a distinct shade of blue, while with three or four times this proportion the reaction is wholly beyond question.

On the other hand, a blue coloration of bread and flour by an ammoniacal solution of logwood does not infallibly prove the presence of a soluble aluminium compound, as several other mineral additions produce a somewhat similar reaction.

small strips of gelatin in the liquid. After twelve hours the gelatin strips are removed and immersed in the alkaline solution of logwood, when, if alum be present, they acquire a blue colour of a much more decided tint than is obtainable from the original sample. If desired, the gelatin strips may be washed, dissolved in hot water, and the absorption-spectrum of the solution observed.

869. *Determination of Alum in Bread.*—Of the constituents of alum, the element most generally of service for its determination in bread is the aluminium. Pure wheat grain appears to be wholly destitute of aluminium compounds, but commercial wheat flour to which no alum has been added is apt to contain small but sensible traces of aluminium derived from extraneous mineral matter. Such aluminium is present as silicate, and gives no blue colour with the logwood test. On the other hand, all the ordinary methods of quantitatively estimating the alum are incapable of distinguishing between the aluminium present as silicate and that existing in a soluble form. Hence it is usual to make a correction for the aluminium present as silicate. This is difficult to do with any approach to accuracy, but it may be taken as a rule that from the amount of alum calculated from the total aluminium in the bread should be subtracted a weight equal to the silica found, when the difference will be approximately the true amount of alum added.

870. The following method should be employed for the determination of the total alumina and silica in bread :—100 grammes' weight of the sample is dried at 100° C., and then incinerated. This is best done by heating it in a platinum tray (about 5 inches by 3) in a gas-muffle, but may also be effected in a platinum dish or large crucible placed over a bunsen. The heat should be moderate, so as to avoid fusion of the ash. The process is completed by adding pure sodium carbonate and a little nitre, and heating the mixture to fusion. The product is rinsed out with water into a beaker, acidulated with hydrochloric acid, and evaporated to dryness. The residue is taken up with dilute acid, and the liquid filtered from the silica, which is washed, dried, and weighed. To the solution, dilute ammonia is added till the precipitate barely redissolves on stirring, when a slightly acid solution of ammonium acetate is added, and the liquid raised to the boiling point. After a few minutes' heating the solution should be set aside for some hours, when its appearance should be observed.[1] The precipitate of

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[1] If gelatinous, it probably consists solely of iron and aluminium phosphates, but if granular more or less of the earthy phosphates have probably been coprecipitated. In such a case the precipitate should be separated, redissolved in dilute hydrochloric acid, and the solution again neutralised with ammonia, and treated with ammonium acetate.

iron and aluminium phosphates should be filtered off, washed, and redissolved in the smallest possible quantity of hydrochloric acid. The resultant solution is poured into an excess of an aqueous solution of *pure* caustic soda contained in a platinum or nickel vessel. After heating for some time, the liquid is considerably diluted and filtered. The filtrate is acidulated with hydrochloric acid, ammonium acetate and a few drops of sodium phosphate added, and then a slight excess of ammonia. The liquid is kept hot till all smell of ammonia is lost, when it is filtered, and the precipitated aluminium phosphate washed, ignited, and weighed. Its weight, multiplied by 3·713, gives the ammonium alum, or by 3·873 the potassium alum in the 100 grammes of bread taken. The amount so found requires a correction equal to the percentage of silica obtained.[1] By multiplying the percentage of alum by 280, the number of grains of alum per 4 lb. loaf will be obtained. The number of milligrammes of $AlPO_4$ per 100 grammes of bread gives, without calculation, a close approximation to the number of grains of ammonium alum per 4 lb. loaf.[2]

Throughout the foregoing process the use of porcelain vessels should be wholly avoided, and care should be taken that the alkaline liquids are not heated in glass. The caustic soda employed should be scrupulously free from alumina.

871. *Plaster of Paris* has been found in flour by Fairley, and has been met with by the author in muffins to the extent of 1 per cent. of their weight. In oat-cake it is said to be occasionally present to the extent of 10 per cent. and upwards. From flour, plaster of Paris is readily separated by treatment with chloroform.

The presence of plaster of Paris in bread is recognised by the high total ash, and the high proportion of calcium contained in it. The sulphates of the ash do not afford a means of accurately determining the amount of plaster present, as the albuminoids furnish a notable quantity of sulphates on igniting the cereals. On the other hand, mere traces of sulphates exist ready formed in the cereals, and hence their determination in the unignited bread affords a means of estimating the plaster present. This method, though theoretically perfect, presents some difficulties in practice, owing to the difficulty of obtaining a solution of the sulphates fit for precipitation with barium chloride. The best way is to soak 12·20 grammes of the bread for some days in 1200 c.c. of cold distilled water till mould commences to form on the surface of the liquid. The solution is strained through coarse muslin, and the filtrate treated with 20 c.c. of carbolic acid distilled over a small quantity of lime. The whole is then raised to the boiling point and filtered through paper. 1 litre of the filtrate is then slightly acidulated with hydrochloric acid, and precipitated in the cold by barium chloride. 237 parts of $BaSO_4$ represent 136 of plaster of Paris. Experiments conducted in the author's laboratory with the view of testing the accuracy of this process gave very satisfactory results.

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[1] The writer has endeavoured to devise a method of extracting alumina from bread in such a manner as to render unnecessary the questionable correction for the aluminium existing as silicate. Very encouraging results were obtained by a process based on the solution of the starch by malt extract, destruction of the soluble carbohydrates by yeast, acidulation of the liquid by nitric acid, followed by filtration, evaporation of the liquid, ignition of the residue, and precipitation of the aluminium as phosphate in the usual way.

A. Wynter Blyth has extracted the greater part of the aluminium of the alum by soaking the bread in dilute hydrochloric acid.

[2] At the present time ammonium alum is almost unknown in the market, while for some years it was equally difficult to meet with potassium alum.

872. *Sulphate of Copper* was formerly employed as an adulterant of bread, especially in foreign countries, and a recent instance of its employment in this country has been recorded by W. F. Lowe (*Analyst*, ix. 109). This objectionable addition can be detected, even when present in but very minute proportion, by soaking the bread in a solution of potassium ferrocyanide acidulated with acetic acid, when a purplish or reddish-brown coloration will be produced if copper be present. The amount of copper may be determined by moistening 100 grammes of the bread with sulphuric acid, igniting, and estimating the metal in the ash.

873. Very minute proportions of copper have been stated to exist normally in wheat-ash, but it is doubtful whether its presence was not due to the practice, formerly very common, of steeping the corn in a solution of copper before sowing it (see E. F. Willoughby, *Analyst*, viii. 83).

874. Organic Adulterants in *flour* are best detected by the microscope, but in *bread* the process of baking so alters the structure of the starches as to render the microscopic indications of very little value.

For the detection of certain additions to flour, A. E. Vogl shakes 2 grammes of the sample with 10 c.c. of alcohol at 70 per cent., to which $\frac{1}{20}$th of hydrochloric acid has been previously added. Both the colour of the flour and that of the liquid are then observed, but the reaction is often developed only on standing, and in other cases is promoted by heating. Pure wheat or rye-flour remains white, and the liquid also remains colourless, or shows merely a yellowish tint in the case of coarse qualities. Pure barley and oatmeal give a straw-yellow liquid.

Corn-cockle[1] colours the liquid a full orange, pea-flower an orange-red, and vetches and beans give a fine purple-red colour. Mildewed wheat is said to give a purple-red, and ergotised wheat a blood-red coloration. According to C. Hartwich, the presence of rhinanthine in flour or bread may be detected by boiling an alcoholic solution of the sample with hydrochloric acid, when the liquid will assume an intense green colour on cooling, if rhinanthine be present.[2]

Some admixtures, such as haricot beans, are stated to give a coloration varying from orange-yellow to very dark-green on mixing the meal with a dilute solution of ferric chloride, while pure wheat flour only acquires a pale straw colour when similarly treated.

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[1] Corn-cockle occasionally occurs in cereals to a considerable extent. It imparts a bitter taste to the bread, and is said to be injurious. If the meal be passed through a sieve having meshes 1 millimetre in diameter, the corn-cockle husks will remain on the sieve and be recognisable by their dark colour. The starch-granules of the corn-cockle are very small (about 0·006 millimetre in diameter), but not otherwise characteristic. Petermann suggests that corn-cockle should be sought for by digesting 500 grammes of the meal in a litre of 85 per cent. alcohol, and filtering the solution whilst hot. The filtrate is precipitated by addition of absolute alcohol, the precipitate dried, and taken up by cold water. This extract is again precipitated by alcohol, the precipitate dried, when, if of a yellowish-white colour, bitter burning taste, and soluble in water, it consists of saponin derived from corn-cockle.

[2] Rhinanthine is a glucoside occurring in the seeds of the yellow rattle (*Rhinanthus crista galli*), a plant often found mixed with rye.

ACID DERIVATIVES OF ALCOHOLS, AND VEGETABLE ACIDS.

875. This numerous and important class of organic bodies contains a great variety of acids, some of which occur ready-formed in plants, and the synthesis of which has not been hitherto effected in the laboratory. In addition to these, there are many which can also be obtained artificially, and others again which are purely artificial products.

876. All the acids treated of in this division are compounds of carbon, hydrogen, aud oxygen. When a metallic salt of one of them is ignited in the air it leaves the metal, sometimes in the free state (as the salts of silver) but more frequently in the form of oxide. If the organic salt be a compound of one of the metals of the alkalies or alkaline-earths, on ignition in the air the corresponding carbonate is obtained. If this be dissolved in standard acid, the diminution in the acidity of the liquid will be equivalent to the organic acid previously present. This fact is often utilised for the indirect determination of vegetable acids (see methods *c* and *e*, par. 889), and is applicable in presence of sulphates, chlorides, &c. The substance or solution must be neutral in reaction before ignition, or, if not so, must be brought into that condition. Nitrates interfere, as, on ignition in contact with organic matter they yield carbonates, together with decided traces of cyanides.

877. The following table shows the manner in which the neutral solutions of the potassium or sodium salts of the acids of this division are precipitated by cold neutral solutions of barium, calcium, and ferric chlorides, by lead acetate, and by silver nitrate. In all cases, the reactions refer to moderately concentrated solutions of the salts. When the precipitate is somewhat soluble in water, so as to render its production questionable, the letter P is placed within parentheses. S signifies that the substance formed is soluble, and hence that no precipitate is obtained. Except

when otherwise mentioned the precipitates are white. In addition to the reactions with the above metallic solutions, columns are added showing the reactions of the organic acids with other important reagents. R signifies "Reduction," and 0 "no effect":—

TABLE SHOWING THE REACTIONS OF NEUTRAL SOLUTIONS OF VEGETABLE ACIDS WITH REAGENTS.

Name of Salt in Solution.	With Barium Chloride.	With Calcium Chloride.	With Ferric Chloride.	With Lead Acetate.	With Silver Nitrate.	With Hot Fehling's Solution.	With Permanganate in Cold Acid Solution.	With Hot Concentrated Sulphuric Acid.	Remarks.
Acetate, .	S	S	Red colour.	S	(P)	0	...	Smell of acetic acid.	Ag salt not reduced on heating solution.
Formate, .	S	S	Red colour.	S	(S)	...	R	CO evolved.	Ag salt or solution reduced on heating.
Oxalate, .	P	P	S	P	P	0	R	$CO+CO_2$ evolved.	A yellow precipitate sometimes occurs on adding $FeCl_3$.
Lactate, .	S	S	S	S	S	0	R	CO evolved, brown colour.	See "Lactic Acid."
Succinate,	(P)	(S)	Red-brown precipitate.	P	P	0	0	No change.	Ba and Ca salts precipitated on adding alcohol.
Malate, .	S	(S)	S	P	P	0	R	Darkened.	Ca salts insoluble in dilute alcohol.
Tartrate, .	P	P	S	P	P	0	R	Charring.	Ag salt reduced on heating.
Citrate, .	P	P	S	P	P	0	0	CO evolved brown colour.	Ca salt precipitated on boiling and redissolved on cooling.
Aconitate,	(P)	(P)	...	P	P	...	...	...	Ca salt is soluble in 100 parts of water.
Meconate,	(P)	P	Red colour.	P	P	...	...	...	Action of oxidising agents not recorded.
Gallate,[1] .			Blue-violet turning green.	P	Reduced on heating.	0	R	Violet-red colour.	Salts darken rapidly in presence of alkali.
Pyrogallate,			Blue-violet turning wine-red.	P	Reduced in the cold.	R	R	Chars when strongly heated.	Salts darken rapidly in presence of alkali.
Gallotannate,[1]			Blue-black precipitate.	P	Reduced on heating.	R	R	Dull purple colour and charring.	Almost impossible to obtain neutral solutions.

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[1] Gallic and gallotannic acids properly belong to the class of vegetable acids, but their analytical characters will be described at length with greater convenience in a separate section. Pyrogallic acid is merely a product of the action of heat on gallic acid, and does not occur naturally.

878. ACETIC ACID.

Hydrogen Acetate.

French—Acide acétique. *German*—Essigsaure.

$$C_2H_4O_2 = H,C_2H_3O_2 = \left.\begin{matrix}C_2H_3O_2\\ H\end{matrix}\right\}O = \left\{\begin{matrix}CH_3\\ CO.OH\end{matrix}\right. .$$

Acetic acid exists ready formed in certain plants, and is a frequent product in chemical reactions. It is produced by the acetic fermentation of sugar, and by the limited oxidation of alcohol. In commerce, the largest quantity is obtained from the products of the distillation of wood, in the manner described under "pyroligneous acid (par. 890).

879. Pure acetic acid is a colourless liquid, having a strongly acid and pungent smell and taste. On cooling, it crystallises in large transparent tables which melt at 16·7° C., and hence the absolute acid is known as "glacial acetic acid." Like many of its salts, acetic acid exhibits the property of super-fusion very readily, remaining liquid if cooled down in a closed vessel, even below 0°, but on opening or shaking the vessel, or dropping in a fragment of the solid acid, the whole solidifies, and the temperature rises to 16·7°. A small addition of water lowers the melting point of acetic acid very considerably, so that an acid containing 13 per cent. of water melts below 0°, and one containing 38 per cent. of water (corresponding to $C_2H_4O_2 + 2H_2O$) has a melting point of $-24°$ C. If still more water be added the melting point again rises.

880. Absolute acetic acid boils at 119° C. and distils unchanged. In distilling hydrated acid the last fractions are absolute or nearly so. For peculiarities in the strength of distilled acetic acid see par. 926, *e*.

881. Addition of water to glacial acetic acid causes evolution of heat, and a contraction in volume ensues till the mixture contains about 23 per cent. of water, probably owing to the formation of a hydrate of the composition, $C_2H_4O_2,H_2O$. Acid of this strength has a higher density than the glacial acid, so that either concentration or dilution causes a diminution of gravity. This fact must not be lost sight of in estimating acetic acid by its density. In fact, the density is not to be relied on for the determination of acetic acid in concentrated solution, though it is of service for the dilute acid.

882. The densities of mixtures in various proportions of acetic acid and water have been determined by Mohr and by Oudemanns. According to the latter chemist, Mohr's observations were made on an acid containing 5 per cent. of water.

The following table shows the density of acetic acid of different strengths, according both to Oudemanns and to Mohr, the temperature in each case being 15° C. (=59° F.):—

$C_2H_4O_2$ per cent.	Density.		$C_2H_4O_2$ per cent.	Density.	
	Oudemapns.	Mohr.		Oudemanns.	Mohr.
1	1·0007	1·001	21	1·0298	1·029
2	1·0022	1·002	22	1·0310	1·031
3	1·0037	1·004	23	1·0324	1·032
4	1·0052	1·005	24	1·0337	1·033
5	1·0067	1·007	25	1·0350	1·034
6	1·0083	1·008	26	1·0363	1·035
7	1·0098	1·010	27	1·0375	1·036
8	1·0113	1·012	28	1·0388	1·038
9	1·0127	1·013	29	1·0400	1·039
10	1·0142	1·015	30	1·0412	1·040
11	1·0157	1·016	31	1·0424	1·041
12	1·0171	1·017	32	1·0436	1·042
13	1·0185	1·018	33	1·0447	1·044
14	1·0200	1·020	40	1·0523	1·051
15	1·0214	1·022	50	1·0615	1·061
16	1·0228	1·023	60	1·0685	1·067
17	1·0242	1·024	70	1·0733	1·070
18	1·0256	1·025	77	1·0748	1·0735
19	1·0270	1·026	80	1·0748	1·0735
20	1·0284	1·027	90	1·0713	1·0730
			100	1·0553	1·0635

From this table it will be seen that acid of 100 per cent. and acid of about 43 per cent. have the same density.

883. The "Acetic Acid" of the British Pharmacopœia contains 33 per cent. by weight of real acid ($C_2H_4O_2$), and has a density of 1·044.

884. "Dilute Acetic Acid," B.P., made by diluting one measure of the above with seven of water, has a gravity of 1·006, and contains 4·27 per cent. of real acetic acid ($C_2H_4O_2$).

885. The "Glacial Acetic Acid" of the Pharmacopœia is said to have a density of 1·065 to 1·066, and to contain at least 98·8 per cent. of real acid.[1] It should crystallise at 1·1° C. (=34° F.), and remain solid till heated above 8·9° C. (=48° F.).

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[1] If Oudemanns' density table be correct, these characters are incompatible. All the B.P. percentages appears, however, to be calculated from Mohr's table. On the other hand, the writer has shown (*Analyst*, iii. 268) that inconsistencies exist in the part of Oudemanns' tables referring to dilute acids,

886. Absolute acetic acid is miscible in all proportions with water, alcohol, and ether. It dissolves many essential oils, camphor, and resins, phenols, gelatin, and many metallic salts insoluble in water.

Cold acetic acid is not inflammable, but the vapour given off by the boiling liquid burns with a blue flame. The strong acid is a powerful caustic. It does not redden litmus until mixed with water.

887. Acetic acid is a very stable body. The most powerful oxidising agents attack it with difficulty. Chromic acid has no effect on it, and a solution of chromic acid in glacial acetic acid is employed for the oxidation of anthracene and other hydrocarbons. Nitric acid has no reaction on acetic acid; chlorine converts it into chloracetic acid, H,C_2H_2ClO,O.

Acetic acid forms an important class of salts called acetates, some of which are described in par. 920 *et seq.*

888. Detection of Acetic Acid and Acetates.

Most of the acetates are soluble in water. A few oxy-acetates ("basic" acetates) are insoluble, and the neutral argentic and mercurous salts are sparingly soluble. Hence, acetic acid cannot be determined or readily detected by precipitation. Free acetic acid may generally be recognised by its smell and other physical properties, or it may be neutralised by caustic soda, and examined by the following tests:—

Metallic acetates give the following reactions:—

a. Subjected to dry distillation, acetone, C_3H_6O, is given off, having a highly characteristic odour (see par. 126).

b. Heated in the solid state in admixture with arsenious oxide (As_2O_3), acetates give an alliaceous and very characteristic smell of cacodylic oxide, which body is very poisonous.

c. Heated with sulphuric or phosphoric acid, acetic acid is evolved.

d. Heated with rectified spirit of wine (not methylated) and concentrated sulphuric acid, a fragrant and characteristic odour of ethyl acetate (acetic ether) is produced (see par. 296).

e. The neutral solution, on treatment with ferric nitrate or chloride (*avoiding excess*), gives a deep-red liquid containing ferric acetate. This is decomposed on boiling, the liquid becoming colourless and depositing reddish-brown ferric oxy-acetate. The reaction is imperfect if the iron solution be added in excess. The cold red liquid is not decolorised on addition of mercuric chloride (distinction between acetates and thiocyanates), and is not

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though it is decidedly preferable to Mohr's. Of course these discrepancies are quite independent of the well-known abnormal density of acetic acid of a certain strength.

taken up by ether on agitation (distinction from thiocyanates); but the colour is readily destroyed on addition of cold dilute sulphuric or hydrochloric acid (distinction from meconates).

f. Insoluble or *basic* acetates may be decomposed by boiling solution of sodium carbonate, when the acetate will be found in the filtered liquid as a sodium salt.

Acetates of alkaloids and nitrogenised *organic bases*, as a rule, respond to the foregoing tests, but acetates of the *alcohol radicles* (acetic ethers) do not usually do so. The latter are readily decomposed, however, by digestion with alcoholic potash or soda, and, after distilling off the resultant alcohol, the residual liquid may be examined for the acetate of an alkali-metal (see also "Compound Ethers," par. 291).

889. DETERMINATION OF ACETIC ACID AND ACETATES.

a. When simply in admixture with water, acetic acid may be determined by the density of the liquid (see par. 882).

b. In the absence of other free acids, free acetic acid may be determined volumetrically, by titrating the liquid with decinormal alkali. Litmus solution may be used as an indicator, or, when dark-coloured liquids are to be assayed, litmus *paper* may be substituted for it.

A preferable indicator to litmus is to be found in phenolphthaleïn, as acetate of sodium is quite neutral to it, while alkaline to litmus. The end-reaction is very sharp. Highly coloured liquids, such as vinegar, may be largely diluted before titrating, as the delicacy of the reaction suffers but little from such treatment.

Methyl-orange and phenacetolin are not suitable indicators for titrating acetic acid, and with rosolic acid the end-reaction is indistinct.

c. Like the corresponding salts of other organic acids, the acetates of the metals of the alkalies and alkaline-earths are converted into carbonates on ignition. Hence, in the absence of other organic acids, or of nitrates, &c., the amount of acetate originally present may be ascertained by titrating the residue of the ignition with standard acid. Each c.c. of normal acid required for neutralisation represents ·060 grammes of $C_2H_4O_2$ in the sample.

d. The acetates of such metals as are completely precipitated by sodium carbonate (*e.g.*, calcium, lead, iron) may be decomposed by a known quantity of it, the liquid well boiled, filtered, and the filtrate titrated with standard acid. The loss of alkalinity represents the acetic acid originally present as an acetate. Before employing this method, the solution must be exactly neutralised, if not neutral already.

e. In presence of salts of inorganic acids, the last method is valueless, but the following modification may be employed :—The excess of carbonate of sodium is exactly neutralised by hydrochloric acid, the liquid evaporated to dryness, the residue gently ignited, and the resultant carbonate titrated with standard acid. Each c.c. of standard acid used represents ·060 grammes of acetic acid. Other organic acids will be estimated as acetic acid.

f. Free acetic acid may also be determined by adding excess of pure precipitated barium carbonate to the solution. The liquid is well boiled, filtered, and the barium in the filtrate precipitated by dilute sulphuric acid. 233 parts of $BaSO_4$ obtained, represent 120 of $HC_2H_3O_2$ in the sample taken. This process is applicable in presence of oxalic, phosphoric, sulphuric, and other *free* acids forming insoluble barium salts, but is useless in presence of soluble oxalates, phosphates, sulphates, &c. The method is available in presence of alkaline chlorides, &c., but not in presence of free hydrochloric acid, unless the solution be previously treated with excess of argentic sulphate. Acetates and chlorides of metals of the alkalies and the alkaline-earths do not interfere, but acetates and other salts of iron, aluminium, and other metals precipitable by barium carbonate must be absent.

g. Weigert determines the free acetic acid in wine, by distilling four or five times to dryness under greatly reduced pressure, and titrating the distillate.

h. The determination of acetic acid in acetates is best effected by distilling the salt to dryness with a moderate excess of sulphuric acid, or with acid sodium sulphate. Water should then be added to the contents of the retort, and the distillation repeated. A third, and even a fourth, distillation will sometimes be necessary, as the last traces of acetic acid are volatilised with extreme difficulty.

In presence of hydrochloric acid or chlorides, excess of sulphate of silver should be added before commencing the distillation.

In presence of sugar or other bodies liable to decomposition by sulphuric acid, phosphoric acid should be substituted for the latter. Care should be taken that the phosphoric acid used is free from nitric and other volatile acids. This is best ensured by adding a little ammonia, and heating the acid to fusion in a platinum crucible.

This plan is of service for the determination of acetic acid in wine. A measured quantity of the sample is neutralised with baryta, the alcohol distilled off, phosphoric acid added to the residue, and the distillation repeated, the process being carried nearly to dryness. To obtain the last traces of acetic acid, water should be added and the distillation repeated.

For the determination of acetic acid in presence of its homologues, see par. 926.

890. Pyroligneous Acid.

French—Acide Pyroligneux, or Vinaigre de Bois. *German*—Holz-essig, or Holz-säure.

Pyroligneous acid or wood-vinegar is the crude acetic acid obtained by the distillation of wood. It is a very complex product, containing, besides acetic acid, all the homologues of acetic acid from formic to caproic acid; crotonic and angelic acids; furfurol; bodies of indefinite nature called "wood-oils"; pyrocatechol and creasol; acetone, and other ketones of the acetic and oleic series; methyl alcohol and the other constituents of wood-spirit; &c. By neutralising the crude product with lime and distilling, the volatile substances of indifferent nature are removed. When partially concentrated, the solution is faintly acidulated with hydrochloric acid, when creasote and various tarry matters separate out; and the clear liquid on evaporation to dryness yields a brownish residue, which is heated to about 230° C. to decompose the empyreumatic products. On distillation with hydrochloric acid a comparatively pure acid may be obtained, which can be further purified by rectification with a little potassium bichromate. A better product is said to be obtainable by converting the acid into a sodium salt, heating to destroy tarry matters, and distilling with hydrochloric or sulphuric acid.[1]

891. Pyroligneous acid varies much in strength according to the kind and state of division of the wood used for distillation, and is also affected by the construction of the retorts. Lopwood yields stronger acid and less tarry and resinous matters than spent dye-woods and sawdust, even though the same kind of wood be employed.

Pyroligneous acid from finely-divided wood has a density of 1·040 to 1·045, and contains, on an average, about 4½ per cent.

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[1] The empyreumatic flavour which clings so persistently to acetic acid derived from the dry distillation of wood, is in great measure due to the presence of furfuraldehyde or furfurol, $C_5H_4O_2$, vapours of which are always produced if a warm mixture of sulphuric acid and water be poured on bran or sawdust, or if bran be distilled with an equal weight of sulphuric acid and three parts of water. If the vapours of furfurol be evolved in a beaker covered with filter paper soaked in aniline, the latter will acquire a fine red colour, which, however, soon disappears. This reaction may be employed for the detection of furfurol, which may be removed from pyroligneous acid by agitating the liquid with 2 or 3 per cent. of benzene. The aqueous layer, after separation from the benzene, is stated to give, by a single distillation, a very palatable table-vinegar.

of real acetic acid ($H,C_2H_3O_2$). The product of the distillation of lop-timber contains an average of 7¾ per cent. of real acid.

892. The strength of pyroligneous acid may be ascertained by titration with standard alkali and phenolphthaleïn, but the liquid is frequently too dark in colour to permit of the end-reaction being readily observed (see par. 889, *b*). Sulphates and acetates of calcium and sodium are frequently present. In the absence of sulphates, pyroligneous acid is best assayed by treatment with excess of barium carbonate, with estimation of the dissolved barium as sulphate (par. 889, *f*).

893. **Commercial Acetic Acid** varies in strength from the nearly absolute glacial acid to the weakest vinegar. The proportion of real acetic acid may be ascertained by the methods already described (par. 889); in certain cases by the density; and in the case of glacial acid by the solidifying point.

The assay of glacial acetic acid, pyroligneous acid, and vinegar is described in the respective sections treating of these products.

894. Commercial acetic acid is commonly prepared by distilling the acetate of sodium or calcium with sulphuric or hydrochloric acid. It is liable to contain the following impurities:—

Sulphuric Acid and Sulphates, indicated and determined by addition of barium chloride, which in their presence throws down white barium sulphate.[1]

Sulphurous Acid, indicated by adding barium chloride in excess, filtering from any precipitate, and adding bromine water to the clear filtrate. An additional precipitate of barium sulphate indicates the previous presence of sulphurous acid, and from its weight the amount of impurity can be calculated.

Hydrochloric Acid and Chlorides, detected and estimated by addition of nitrate of silver.

Copper and Lead, detected by evaporating a considerable bulk of the sample to a small volume, diluting with water, adding a few drops of hydrochloric acid, and passing sulphuretted hydrogen, which produces a black or brown coloration or precipitate in presence of lead or copper. If much organic matter be present, the evaporation should be carried to dryness, and the residue ignited in porcelain. The heavy metals are then sought for in the residue in the manner described in par. 104. A delicate test for copper is the red-brown precipitate or coloration produced by potassium ferrocyanide in the original liquid, or the same concentrated and then diluted with water. If iron be present in such quantity as to give a blue precipitate and thus interfere with the reaction, it must first be removed by addition of bromine water and excess of ammonia, and copper sought for in the filtrate after acidifying with acetic or hydrochloric acid. Samples of pickles suspected to be coloured with copper should be moistened with sulphuric acid, ignited, and the ash dissolved in nitric acid, and tested in acid solution with potassium ferrocyanide, after separation of the iron and phosphates with ammonia. The copper can be determined by electro-deposition on the inside of a platinum crucible by a current from one cell of Grove's battery, or by precipitation with a stick of cadmium. *Tin* and *zinc* have been occasionally met with in acetic acid and vinegar (see pars. 104 and 917).

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[1] For the detection and estimation of small amounts of free sulphuric and hydrochloric acids in acetic acid and vinegar, see page 390 *et seq.*

Salts of Calcium are detected by partially neutralising the solution with ammonia and adding ammonium oxalate, which will produce a white precipitate of calcium oxalate.

Empyreumatic and Indefinite Organic Bodies may be detected by exactly neutralising the acid with sodium carbonate and tasting and smelling the warmed liquid. The neutralised acid gives a precipitate when heated to boiling with ammonio-nitrate of silver, and the original acid darkens when heated to boiling with an equal measure of concentrated sulphuric acid, if the above impurities are present.[1] A comparative estimate of the proportion of empyreumatic impurities present may be made by diluting 10 c.c. of the sample to 400 c.c. with water, adding hydrochloric acid, and titrating with permanganate till the pink colour is permanent for one minute.

General Fixed Impurities are detected and estimated by evaporating of a known measure of the sample to dryness and weighing the residue.

895. Glacial Acetic Acid (Absolute Acetic Acid). The properties of this substance have been already described (page 379).

Commercial glacial acetic acid should contain at least 97 per cent. of the absolute acid. This may be ascertained by agitating 1 volume of the sample with 9 of oil of turpentine. Complete solution occurs if the strength is 97 per cent. or above. Samples containing 99·5 per cent. of absolute acid are miscible with oil of turpentine in all proportions. Oil of lemon, if freshly distilled, may be employed instead of turpentine.

A more delicate test for water is to treat the sample in a dry test-tube with an equal measure of carbon disulphide, and warm the mixture in the hand for a few minutes. The liquid will be turbid if any water be present in the sample.

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[1] A sample of glacial acetic acid containing fully 99 per cent. of $C_2H_4O_2$ was observed by V. Meyer to give a deep red coloration with aniline. This property he traced to the presence of furfurol (see footnote on page 384), and from the depth of the coloration produced estimated the proportion of the impurity to be 0·108 grammes per litre of the acid.

896. The influence of various proportions of water on the melting point of glacial acetic acid is shown in the following table by Rudorff (*Pharm. Jour.* [3], ii. 241).

Solidifying Point. ° C.	Water to 100 parts of real $C_2H_4O_2$.	Solidifying Point. ° C.	Water to 100 parts of real $C_2H_4O_2$.
+16·70	0·0	6·25	8·0
16·65	0·5	5·30	9·0
14·80	1·0	4·30	10·0
14·00	1·5	3·60	11·0
13·25	2·0	2·70	12·0
11·95	3·0	−0·20	15·0
10·50	4·0	−2·60	18·0
9·40	5·0	−5·10	21·0
8·20	6·0	−7·40	24·0
7·10	7·0		

The strength of glacial acetic acid may also be determined as in par. 889. The density is not an indication of value. Impurities may be sought for as in par. 894.

897. Vinegar.

French—Vinaigre. *German*—Essig.

Properly speaking, vinegar is a more or less coloured liquid, consisting essentially of impure dilute acetic acid, obtained by the oxidation of wine, beer, cider, or other alcoholic liquid. Sometimes the term is improperly extended to pyroligneous acid, or "wood-vinegar," while acetic acid is called "distilled vinegar."

898. The acetification of alcohol appears to occur in two stages, the first resulting in the formation of aldehyde, C_2H_4O, while this is further changed to acetic acid, $C_2H_4O_2$.[1] Both reactions require the presence of free oxygen, and in practice they occur simultaneously. Although the reaction between alcohol and atmospheric oxygen takes place under the influence of platinum-black and certain other bodies, the formation of vinegar from alcoholic liquids appears in practice to depend on the presence of an organised ferment called the *mycoderma aceti.* Various mechanical arrangements are employed to expose a large surface of the alcoholic liquid to the air, so as to diminish the time required for acetification.

899. Besides acetic acid, vinegar often normally contains more or less of other organic acids, sugar, dextrin, colouring matters, &c. The agreeable aromatic smell is doubtless due to characteristic ethers, and is sometimes imitated by direct addition of ethyl acetate.

[1] $C_2H_6O + O = C_2H_4O + H_2O$; and
$C_2H_4O + O = C_2H_4O_2$.

900. The "Vinegar" of the British Pharmacopœia has a density of 1·017 to 1·019, and contains at least 5·4 per cent. by weight of absolute acetic acid ($C_2H_4O_2$). The specific gravity of vinegar is of no value as an indication of its strength in acetic acid, as the proportion of extractive matter varies much in vinegar from various sources.[1] The "proof vinegar" of the Excise contains about 5 per cent. of acetic anhydride ($C_4H_6O_3$), or 6 per cent. of the absolute acid, and has a density of 1·019. By the manufacturer, vinegars of different strengths are distinguished by the number of grains of pure dry carbonate of sodium required for the neutralisation of one fluid ounce. Thus "proof vinegar" is known as "No. 24," from the fact that 24 grains of Na_2CO_3 are required for the neutralisation of one ounce. The weaker qualities are Nos. 22, 20, and 18. As 60 grains of absolute acetic acid, or 51 of acetic anhydride, are neutralised by 53 of sodium carbonate, the number of grains of the real acid contained in each fluid ounce of the vinegar can be ascertained by multiplying the "number" of the sample by $\frac{53}{50}$ = 1·132. If the "number" be multiplied by the factor ·259, the product will be the parts by weight of absolute acid ($C_2H_4O_2$) in 100 measures of vinegar.

The vinegar of the German Pharmacopœia is required to contain at least 6 per cent. of absolute acetic acid. In Russia the minimum limit of strength is 5 per cent.; in Austria, 6; in Belgium, 5·6; in France, 8 to 9; and in the United States, 4·6 per cent.

Hence it may be asserted that genuine vinegar of good quality does not contain much less than 5 per cent. of absolute acetic acid, though something depends on the origin of the vinegar, cider-vinegar being naturally the weakest and wine-vinegar the strongest in acetic acid. Vinegar containing less than 3 per cent. of real acetic acid may be regarded as diluted with water, or at any rate as unfit for use.

The proportion of acetic acid in vinegar may be ascertained by titration with standard caustic alkali, litmus-paper or phenolphthaleïn being used as an indicator. Other methods are described in par. 889.

901. Wine-Vinegar varies in colour according as its origin is white or red wine, that derived from the former being most esteemed.

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[1] The excess of density of dilute acetic acid over that of water is said to be doubled on neutralisation with lime. This fact affords a means of roughly assaying vinegar and ascertaining the proportion of extract. Thus, if a sample have a density 1·017, increased to 1024 on neutralisation with lime, then the density of the pure acetic acid present would be 1·007, and that of the "extract" 1·010.

It contains from 6 to 12 per cent. of absolute acetic acid, has a low density (1·014 to 1·022), and an extract varying from 1·7 to 2·4 per cent. (average 2·05). If the "extract" or residue left on evaporation be treated with alcohol, nearly everything dissolves except a granular residue of tartar, while vinegars made from malt or sugar leave a more or less glutinous residue, only sparingly soluble in alcohol. The amount of "tartar" (acid tartrate of potassium) contained in *wine*-vinegar averages 0·25 per cent. Its presence is peculiar to wine-vinegar. The tartar may be proved to be such by pouring off the alcohol and dissolving the residue in a small quantity of hot water. On cooling the aqueous solution, and stirring the sides of the vessel with a glass rod, the acid tartrate of potassium will be deposited in streaks in the track of the rod. An addition of an equal bulk of alcohol makes the reaction more delicate. Tartaric acid is occasionally added to vinegar as an adulterant, in which case the residue left on evaporation at a steam-heat is viscous and highly acid. By treatment with proof-spirit any free tartaric acid is dissolved, and may be detected in the solution by adding a solution of acetate of potassium in proof-spirit, and stirring with a glass rod. In presence of tartaric acid, streaks, and probably a distinct precipitate, of acid potassium tartrate will be produced. By titrating the precipitate with standard alkali, the amount of free tartaric acid in the vinegar can be determined.

902. **CIDER-VINEGAR** is yellowish, has an odour of apples, a density of 1·013 to 1·015, and contains 3½ to 6 per cent. of acetic acid. On evaporation to dryness it yields from 1·5 to 1·8 per cent. of a mucilaginous extract, smelling and tasting of baked apples, and containing malic but no tartaric acid. Cider-vinegar gives slight precipitates with barium chloride, silver nitrate, and ammonium oxalate. Perry-vinegar presents similar characters. Crab-vinegar, made from the crab-apple, is well known in Wales and the adjacent counties.

903. **BEER- AND MALT-VINEGARS** have a high density (1·021 to 1·025), and yield 5 to 6 per cent. of extract, containing a notable proportion of phosphates. The acetic acid varies from 3 to 6 per cent. Barium chloride and silver nitrate frequently give considerable precipitates, owing to the presence of sulphates and chlorides in the water used in the manufacture (see note on page 391).

904. **GLUCOSE- OR SUGAR-VINEGAR** is now extensively prepared from amylaceous materials by conversion with dilute acid, followed by fermentation and acetification. Glucose-vinegar usually contains dextrose, dextrin, and, very often, calcium sulphate (see par.

708). Hence it reduces Fehling's copper solution, and usually gives abundant precipitates with barium chloride and ammonium oxalate, and frequently with silver nitrate also. When mixed with three or four times its volume of strong alcohol, glucose-vinegar gives a precipitate of *dextrin.* It is best to concentrate the sample before applying this test. Dextrose is best detected and determined by evaporating 50 c.c. of the sample to a syrup and adding alcohol. The liquid is filtered, decolorised by boiling with animal charcoal, again filtered, the alcohol boiled off, and the glucose estimated by Fehling's copper solution. Glucose-vinegar is said to be employed in France for adulterating wine-vinegar.

905. ARTIFICIAL VINEGAR is said to be made by mixing wine and acetic acid (often pyroligneous). Such vinegar would give off imflammable vapours of alcohol when boiled. Another factitious vinegar is made by diluting acetic acid to the strength of proof-vinegar, colouring it with burnt sugar, and flavouring it with a little acetic ether. Such a product differs from malt-vinegar by containing no phosphates, and from wine and cider-vinegars in the absence of tartaric acid and malic acid respectively.

WOOD-VINEGAR is a name sometimes applied to pyroligneous acid.

906. AROMATIC VINEGAR is a product obtained by distilling a metallic acetate, usually crystallised cupric acetate. The presence of acetone and other bodies imparts an agreeable aroma. A small addition of camphor or essential oil is often made.

907. MINERAL ACIDS IN VINEGAR.

Very weak vinegar is liable to a putrid fermentation, to prevent which the addition of 1 gallon[1] of sulphuric acid to 1000 gallons of vinegar was permitted by an Excise regulation. This addition is now known to be unnecessary with good vinegar, and is abandoned by the best makers, though the practice is not obsolete, and the legal proportion of sulphuric acid has been occasionally largely exceeded. In addition to sulphuric acid, hydrochloric acid has been occasionally added to vinegar, but the adulteration of vinegar with mineral acids is now very rarely practised.

For detecting mineral acids in vinegar various tests have been devised, but the majority are either untrustworthy or deficient in delicacy. Some are applicable to the detection of sulphuric acid only, whilst others include hydrochloric and other mineral acids also. The employment of barium chloride and silver nitrate, for the detection of sulphuric and hydrochloric acids respectively, has led several analysts into error, owing to the presence naturally of sulphates and chlorides in the water employed in the manufacture of the vinegar.[1]

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[1] This proportion of 1 gallon to 1000 is often erroneously stated at 0·1 per cent., whereas the true proportion resulting from the above admixture is *about* 0·185 parts by weight of sulphuric acid, or nearly twice as much as is generally assumed.

Another circumstance which complicates the problem is that the addition of a mineral acid in moderate quantity merely decomposes the acetates naturally present in the vinegar, with liberation of acetic acid and formation of metallic sulphates or chlorides. Hence, only the *excess* of mineral acid beyond that required for the decomposition of the acetates, &c., can exist in the free state, and to the presence of such *free* mineral acids only can objection reasonably be taken, unless the mineral acid used were contaminated with arsenic.

908. Acetates, and most other salts of organic acids, are decomposed by ignition into carbonates, having an alkaline reaction to litmus, while sulphates and chlorides of the light metals are unchanged on ignition, and possess a neutral reaction. Hence, if the ash of a vinegar have a sensibly alkaline reaction, acetates must have been present in the original vinegar, and therefore no free sulphuric or hydrochloric acid can have been present. To determine the amount of free mineral acid, it is sufficient to carefully neutralise the vinegar with standard solution of soda before evaporation to dryness (the same process serves for a determination of the total free acid), ignite the residue, and titrate the aqueous solution of the ash with standard acid. If the free acid originally present were wholly organic, the ash will contain an equivalent amount of alkaline carbonate, which will require an amount of standard acid for its neutralisation exactly equivalent to the amount of standard alkali originally added to the vinegar. Any

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[1] A remarkable water of this character is employed by Hill & Evans of Worcester. An analysis of it, made in 1874 by Dr Letheby, showed :—

Total solids, ...	266·59	grains per gallon.
Sulphuric acid (SO_3), ...	97·14	,,
Chlorine, ...	48·44	,,
Hardness, ...	123·5	degrees

At the same time, Dr Letheby determined the sulphuric acid and chlorine in two samples of the vinegar in the store-vats at the works, and in a sample of Messrs Hill & Evans' vinegar purchased of a retail dealer at Bedford, and said to be adulterated. The following were the results obtained from the samples in question :—

	Sulphuric Acid (SO_3).	Chlorine.
A. Vinegar from store-vats, .	90·79 grs. per gall.	50·33 grs. per gall.
B. ,, ,, .	92·19 ,,	49·98 ,,
C. Vinegar from Bedford, . .	91·70 ,,	49·42 ,,

deficiency in the amount of standard acid required for neutralisation is due to the *free mineral acid* originally present in the vinegar. More accurate results are obtained if the amount of standard alkali added before evaporation is insufficient for the complete saturation of the acetic acid, but more than enough for the neutralisation of all mineral and fixed organic acids which may be present. By thus proceeding, decinormal alkali and acid may be employed (50 c.c. of the vinegar being used), and thus sharper readings obtained (O. Hehner, *Analyst*, i. 105).

909. The *total chlorine*, existing both as free hydrochloric acid and as metallic chlorides, cannot be determined in vinegar by direct precipitation with silver nitrate, other matters being thrown down simultaneously. For a correct determination, 50 c.c. of the vinegar should be neutralised with alkali, evaporated to dryness, the residue ignited, dissolved in water, and the aqueous solution precipitated with excess of calcium sulphate or nitrate to remove phosphates. The filtrate from this precipitate may be precipitated by, or titrated with, a solution of silver nitrate.

The sulphuric acid and sulphates may be precipitated by the direct addition of barium chloride to the diluted vinegar, but the determination has little value.

910. *Free sulphuric acid*, as distinguished from sulphates, may be determined with considerable accuracy by evaporating 100 c.c. of the vinegar to a small bulk, and then adding to the cold concentrated liquid four or five times its volume of alcohol. Sulphates are precipitated, while free sulphuric acid remains in solution. The filtered liquid is diluted, the alcohol boiled off, and the sulphuric acid precipitated with barium chloride. The precipitate is filtered off, washed, dried, ignited, and weighed. Its weight, multiplied by 0·4206, gives the weight of sulphuric acid (H_2SO_4) in the quantity of vinegar taken. In a vinegar free from chlorides this process gives results in accordance with Hehner's process, but in their presence the mineral acid found is deficient by the amount of sulphuric acid required to decompose the chlorides. This difficulty may be obviated by treating the vinegar with excess of sulphate of silver solution before evaporation, by which treatment any free hydrochloric is also estimated as sulphuric acid (*Analyst*, iii. 290).

911. An ingenious method of detecting *free sulphuric acid* in vinegar and wine has been described by Casali. 20 grammes weight of the sample is ground up in a mortar with about 80 grammes of finely powdered porcelain (previously treated with hydrochloric acid to remove every trace of free alkali), so that the mixture is not moist to the touch. The whole is then ground up

with 50 c.c. of ether (previously agitated with magnesia and water to neutralise any trace of acid) filtered, and washed with ether. The filtrate is then shaken with a little distilled water, the ether distilled off, and the residue precipitated with barium chloride. 0·0005 gramme of free sulphuric acid can be readily detected by this method.

912. A very simple, and apparently reliable, method of detecting free *mineral acids* in vinegar has been described by A. Ashby (*Analyst*, ix. 96). A solution of logwood is prepared by pouring 100 c.c. of boiling water on about 2 grammes of fresh logwood chips, and then allowing the decoction to stand for a few hours. Separate drops of this solution are spotted on the surface of a flat porcelain dish, or on the cover of a porcelain crucible, and evaporated to dryness over a beaker of boiling water. To each spot a drop of the suspected sample (previously concentrated if thought desirable) should be added, and the heating continued till the liquid has evaporated. If the vinegar be pure the residue will be found to have a bright yellow colour, but in presence of a very small proportion of mineral acid the residue assumes a red colour.

If the proportion of mineral acid be very small, the red colour is destroyed on adding water to the residue, but is restored on re-evaporating, except in the case of nitric acid.

913. *Tartaric Acid* in vinegar may be detected as described in par. 901. It is a normal constituent of wine vinegar.

914. *Oxalic Acid* may be detected by evaporating 20 c.c. of the vinegar to a small bulk, diluting the residue with water, and adding calcium acetate solution, or a mixture of acetate of ammonium and chloride of calcium. Any oxalic acid causes the formation of white oxalate of calcium.

915. *Arsenic* has been occasionally met with in vinegar, and may be introduced by the addition of impure hydrochloric or sulphuric acid. It may readily be detected by Marsh's or Reinsch's test.

916. *Lead* and *Copper* may be detected as described in par. 104.

917. *Zinc* is occasionally present in vinegar. It may be detected by boiling down the vinegar to dryness with nitric acid, dissolving the residue in acidulated water, passing sulphuretted hydrogen, filtering from any precipitate, and then adding ammonium acetate, when white sulphide of zinc will be thrown down if the metal be present.[1] A less satisfactory method is to neutralise the greater part of the free acid in the original vinegar

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[1] In presence of iron, the white precipitate may be more or less discoloured, and should be filtered off, dissolved in bromine water, the solution nearly neutralised, boiled with ammonium acetate, filtered, and sulphuretted hydrogen again passed through the filtrate.

by ammonia, and then at once pass sulphuretted hydrogen. Zinc may also be sought for as described in par. 104.

918. *Cayenne Pepper*, *Ginger*, &c., are sometimes added to vinegar to confer pungency. They may be detected by neutralising the concentrated vinegar with sodium carbonate and *tasting* the liquid.

919. Flies (*Musca cellaris*) and "Eels" (*Vibrio eatic*) are often found in vinegar. They are readily detected by the microscope, and may be destroyed by raising the temperature of the liquid to 100° C.

METALLIC ACETATES.

920. Many of these important salts are extensively used in the arts, medicine, &c. Their analytical characters and the general methods adopted for their assay have been, in great measure, described already (pars. 888, 889). The following observations, therefore, have reference chiefly to the detection of impurities and adulterations in commercial acetates of the metals. Sections treating of the acetates of ethyl, amyl, morphine, rosaniline, &c., will be found in other parts of this work.

921. **Potassium Acetate.** $KC_2H_3O_2$. This salt exists in several vegetable secretions. It is deliquescent, very soluble in water and alcohol, and in solution is neutral to test-paper. It undergoes fusion when heated to incipient redness, and at a higher temperature decomposes and leaves a residue of potassium carbonate. The amount of acetate present in commercial samples of the salt may be determined by the general methods given on page 382 *et seq.*

922. COMMERCIAL ACETATE OF POTASSIUM is liable to contain sulphates, chlorides, and carbonates; also salts of iron, lead, copper, and zinc; and arsenic is occasionally present. It is sometimes intentionally adulterated, acetate of calcium, and sulphate, tartrate and carbonate of potassium being employed for the purpose.

Acetate of potassium being readily soluble in rectified spirit, any admixture of *sulphates*, *tartrates*, or *carbonates* may be detected and estimated by treatment with that solvent. *Carbonate* is indicated more precisely by the alkaline reaction of the sample; its precipitation by chloride of calcium; its power of decolorising iodised starch; and by the effervescence produced on adding an acid.

923. **Sodium Acetate**, $NaC_2H_3O_2$, closely resembles the potassium salt, but crystallises with three atoms of water. It is liable to contain the same foreign matters as the acetate of potassium. Crude sodium acetate often contains tarry matters derived from the pyroligneous acid employed in its preparation. Sodium acetate has been employed for preserving meat. Its supersaturated solution has been used for filling railway carriage foot-warmers.

924. **Ammonium Acetate.** $(NH_4),C_2H_3O_2$. This salt is generally met with in solution, but may be obtained in the solid state, when it is apt to contain acetamide, C_2H_3O,NH_2.

Ammonium acetate is liable to contain much the same impurities as the potassium salt, and may be examined in a similar manner. It should be wholly volatile on ignition.

925. **Calcium Acetate.** $Ca''(C_2H_3O_2)_2$. This salt crystallises with difficulty in prismatic needles containing one atom of water. It is decomposed by heat into acetone, C_3H_6O, and calcium carbonate.

Calcium acetate should be completely soluble in water and in proof spirit. An insoluble residue may consist of calcium sulphate, carbonate, &c. The solution should give no precipitate with silver nitrate or barium chloride. Potassium ferrocyanide colours the solution blue if the sample contain iron, and brown if copper be present.

926. ASSAY OF "ACETATE OF LIME."—Calcium acetate is obtained in the manufacture of acetic acid from crude pyroligneous acid. The commercial product is often extremely impure, containing much tarry matter; hydrate, carbonate, and sulphate of calcium; the calcium salts of the homologues of acetic acid, &c.[1] On this account its assay is a matter of some commercial importance, and is not so easily effected as might appear at first sight. Thus, if the salt be ignited, and the amount of acetic acid calculated from the weight of the residual calcium carbonate, or from the amount of normal acid the residue will neutralise, very erroneous results may be obtained.[2]

927. A much used method of assaying crude acetate of calcium is to boil the aqueous solution of the sample with a known amount of carbonate of sodium, and then to filter off the precipitated calcium

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[1] W. Giles informs the writer that formic acid is a very common if not a constant constituent of crude acetate of lime, the proportion of calcium formate sometimes reaching 4 or 5 per cent. When operating on the large scale, the presence of formates is unmistakable. On crystallising out sodium acetate as completely as possible, a dense syrupy liquid is left which contains sodium formate, reduces argentic and mercuric salts, and evolves torrents of carbonic oxide when treated with excess of sulphuric acid.

[2] This is well shown by the following figures given by the late Mr William Baker. The results in column A were obtained by distilling the samples with phosphoric acid, and titrating the distillate with standard alkali. The figures in column B were deduced from the weight of the ash of the sample.

	A. By distillation.	B. By ignition.
No. 1. Calcium acetate, . . .	70·17 per cent.	85·47
No. 2. ,, ,, ...	69·98 ,,	85·30
No. 3. ,, ,, ...	32·29 ,,	73·78

carbonate. The loss of alkalinity found on titrating the filtered liquid represents the amount of acetic acid previously in combination with the lime. This simple process eliminates the error caused by the presence of calcium hydrate or carbonate in the sample, but is liable to give results considerably above the truth, owing to the acid character of some of the tarry matters.

928. A method of assaying calcium acetate, which is much used in the neighbourhood of Manchester, has been communicated to the writer by H. Grimshaw, who finds it very satisfactory. 10 grammes of the sample of crude acetate of lime should be dissolved in boiling water, and 20 grammes of crystallised sodium sulphate added. The liquid is raised to the boiling point, cooled, diluted to 250 c.c., and allowed to stand for six, or preferably for twelve, hours. The calcium will then have separated as a crystalline precipitate of gypsum. The liquid is next filtered, the precipitate washed with hot water, and the filtrate made up to 500 c.c. 50 c.c. of this solution (=1 gramme of the sample) should then be evaporated to dryness at 100°, and somewhat further dried in an air-bath. The residue is ignited at a red heat over a good bunsen burner for half-an-hour,[1] allowed to cool, and treated with 10 c.c. of

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[1] These are Mr Grimshaw's directions. The writer finds a tendency to incomplete decomposition of the acetate if too low a temperature be employed. He prefers to evaporate a measure of solution representing 5 grammes of the sample, and ignite at a moderate red heat in a muffle, subsequently moistening the ash with peroxide of hydrogen to oxidise any sulphides which may have been formed.

A manufacturer of the acetates writes to the author as follows :—"Anybody who has worked out the manufacture of acetate of soda, by decomposing the lime salt with sodium sulphate, is aware that, after all the acetate of sodium that can be crystallised out is obtained, there remains a large quantity of a dark syrupy, tarry liquid, which contains what, in the present state of our knowledge, can only be defined as tarrate of soda, or, at any rate, much of the soda is combined with acid or acids of a non-volatile nature. In the sodium sulphate process of assaying crude acetate of lime all this would be reckoned as acetic acid. If the syrupy liquid be treated with as much or rather more sulphuric acid than is requisite to form $NaHSO_4$ with the soda previously ascertained to be present, and the mixture distilled, only a trifling quantity of volatile acids can be obtained even at a considerable temperature. Yet, if, as is commonly asserted, the mother liquor from the manufacture of sodium acetate is merely a saturated solution of sodium sulphate and acetate, crystallisation of which salts is prevented by the tarry matters present, the greater part of the acetic acid present ought to be recoverable by adding sulphuric acid and distilling; while, as a matter of fact, we get at first only a watery fluid, so weak as not even to pay for the vitriol which is used, followed by torrents of sulphurous acid if the distillation be continued; and, if the whole distillate be rectified over sufficient bichromate of potassium and sulphuric acid to destroy the SO_2, the yield of volatile acid is practically *nil.*"

normal hydrochloric acid, using a cover to avoid loss. The solution is boiled well to drive off carbon dioxide, filtered, the residual carbon washed, and the filtrate titrated with decinormal caustic alkali, using methyl-orange or litmus as an indicator. Each c.c. of normal acid found to have been neutralised by the ash represents 0·060 gramme of acetic acid ($C_2H_4O_2$), or 0·079 gramme of calcium acetate, in the liquid (=1 gramme of the sample) evaporated. Great care is requisite in conducting the titration, as a very small difference in the volume of alkali required makes a sensible change in the result. The portion of the sample taken for the analysis should be finely powdered, and if the solution in water be appreciably alkaline it should be cautiously neutralised with decinormal caustic alkali before adding the sulphate of sodium. Mr Grimshaw finds this process to give results varying from close agreement to about 2 per cent. in excess of those obtained from the same samples by distillation with phosphoric acid.[1] The results are not vitiated by the presence of calcium carbonate or other insoluble calcium compounds in the sample.

929. R. Fresenius has devised a method for the assay of crude acetate of calcium, the details of which are as follow:—5 grammes of the sample are dissolved in water, and mixed with 70 c.c. of normal oxalic acid. The liquid is then diluted with water to 250 c.c., and 2·1 c.c. extra water added to compensate for the space occupied by the precipitated calcium oxalate. The liquid is filtered, and 100 c.c. of the filtrate titrated with normal alkali. In another volume of 100 c.c., the excess of oxalic acid is precipitated with pure calcium acetate, and the precipitate filtered, washed, moistened with sulphuric acid, and weighed. The weight of $CaSO_4$ so obtained, multiplied by ·9265, gives the amount of crystallised oxalic acid in 100 c.c. of the solution (=2 grammes of the sample). By multiplying this result by ·9523 (or the weight of $CaSO_4$ at once by ·882), the equivalent amount of acetic acid is obtained, and by subtracting this figure from the total acidity calculated as acetic

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[1] Mr Grimshaw has suggested the following process as possessing many of the advantages of both the sodium sulphate and the distillation methods of assaying acetate of lime. He treats 10 grammes of the sample with water and excess of "bisulphate" of sodium ($NaHSO_4$), makes up the liquid to a known measure, filters, titrates one portion of the filtrate with standard alkali, and evaporates an equal measure to dryness. The residue is moistened with water, and again dried, this process being several times repeated. The residue is then dissolved and titrated with alkali, when the difference between the volume now required and that employed for neutralising the unevaporated liquid will correspond to the acetic acid in the solution which was evaporated to dryness. Litmus paper is the best indicator.

acid (1 c.c. of normal NaHO = ·060 grammes $HC_2H_3O_2$), the amount of actual acetic acid is found.

930. Calcium acetate may also be assayed by the distillation process, which is preferable on the score of accuracy and being more strictly comparable with results likely to be obtained by the manufacturer, but it is commonly regarded as too tedious a method for general use. This objection is not valid if the manipulation be conducted in the following manner, which is essentially that communicated to the writer by Stillwell and Gladding, and an improvement on their published description:—1 gramme of the sample of acetate of lime is placed in a *small* long necked flask or retort, of a capacity not exceeding 100 c.c., and rinsed in with 15 c.c. of water. The neck of the retort is inclined slightly upwards, and is fitted with a rubber cork, through which passes a bent tube which serves as the inner tube of a Liebig's condenser. The retort is also fitted with a tapped funnel through which is introduced a solution of 5 grammes of glacial phosphoric acid in 10 c.c. of water. This large excess of acid dissolves all the calcium phosphate to a clear liquid. The retort is then heated, and the process continued till the contents are reduced to about 10 c.c., when 25 c.c. of water should be introduced through the funnel and the distillation proceeded with till the liquid in the retort is again reduced to about 10 c.c. The addition of water and re-distillation are repeated three or four times, when the liquid coming over will be found entirely free from acid reaction. The acetic acid in the distillate is then carefully determined by titration with decinormal caustic soda and phenol-phthaleïn, each c.c. of which corresponds to 0·006 gramme (= 0·6 per cent.) of acetic acid ($C_2H_4O_2$) in the sample.[1]

The phosphoric acid employed for the distillation must be free from nitric acid, which if present may be eliminated by adding a little ammonia, and heating the acid to fusion in platinum. If either the phosphoric acid or the sample itself contain chlorides, some sulphate of silver must be added to the contents of the retort. Oxalic acid may be substituted for the phosphoric acid, the solution being filtered from the precipitated calcium oxalate before introduction into the retort. Hydrochloric acid may be used instead, provided that the amount which passes into the distillate be estimated and subtracted from the total acidity as deduced from the titration. Sulphuric acid should not be used, as its reaction on the tarry matters occasions the formation of sulphurous acid, which increases the acidity of the distillate.

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[1] Stillwell and Gladding collect the distillate in a quantity of semi-normal soda not quite sufficient to saturate it, then add enough more to establish a faint alkaline reaction, render just acid with 0·2 c.c. of standard hydrochloric acid, and then boil for fifteen seconds to expel all carbon dioxide. The solution is then brought back to exact neutrality by semi-normal soda, the total amount of which used (less 0·2 c.c. correction for the hydrochloric acid) represents the acetic acid in 1 gramme of the sample.

Stillwell and Gladding recommend that the alkali employed for the titration should be standardised against pure potassium hydrogen tartrate, instead of using a mineral acid.

931. When *pure* calcium acetate is assayed by either of the foregoing methods fairly accurate results may be obtained, but when commercial samples are examined the errors sometimes become very serious. On the whole, the method of distillation with phosphoric acid is the most accurate, but, unless carefully performed, the results are liable to be below the truth, from incomplete volatilisation of the acetic acid, while on the other hand, they may be excessive if nitric or other volatile acid be present in the phosphoric acid used.[1]

As at present manufactured, crude acetate of lime usually contains from 62 to 67 per cent. of calcium acetate, and from 1 to 8 per cent. of insoluble matter, the remainder being water, soluble tarry matters, &c.

932. **Magnesium Acetate.**—The basic acetate of magnesium has been recommended as an antiseptic, and is said to be met with in commerce under the name of "sinodor."

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[1] The following results, obtained some years ago in the writer's laboratory from the *same sample* of "acetate of lime" by different methods, show the nature and direction of the errors to which the various processes are liable :—

	Acetic Acid. Per cent.
By distillation with H_3PO_4, and titration of distillate,	47·4
,, ,, ,, ,, ,,	48·0
,, ,, H_2SO_4, ,, ,,	48·6
,, ,, $H_2C_2O_4$, ,, ,,	48·3
,, ,, ,, ,, ,,	48·4
By Fresenius's method (see par. 929),	53·4
,, ,,	53·2
By ignition and weighing the $CaCO_3$,	53·2
,, and titration of residue,	53·2
,, ,, ,,	53·8
,, ,, ,,	54·0
By boiling with Na_2CO_3, and titrating filtrate,	56·4
,, ,, ,,	56·4
,, ,, ,,	57·6

Improvements in the manufacture of acetate of lime render the discrepancies resulting from the employment of different methods of assay less striking than formerly.

933. **Aluminium Acetate,** $Al'''(C_2H_3O_2)_3$.—This salt is employed in solution by calico-printers, under the name of "red-liquor." It is usually prepared by precipitating a solution of alum or aluminium sulphate by means of calcium or lead acetate, and filtering or syphoning off from the precipitated calcium or lead sulphate. When prepared by means of alum, the product necessarily contains sulphate of potassium or ammonium (according to the kind of alum used), and, as an excess of the precipitant should be avoided, aluminium sulphate is always to be expected. Owing to sulphate of calcium being somewhat soluble in water, it will be met with in red-liquors prepared with acetate of calcium. Such red-liquor is inferior to that prepared by acetate of lead. Good red-liquor contains from 3 to 5 per cent. of alumina, and twice that proportion of acetic acid, and has a density of 1·120, but it is sometimes met with as low as 1·087. Carbonate of sodium is often added to red-liquor to neutralise excess of acid.

934. **Iron Acetates.**—Both ferrous and ferric acetates are employed in the arts. A crude variety of iron acetate is extensively manufactured by dissolving iron in pyroligneous acid.

935. PYROLIGNITE OF IRON, IRON LIQUOR, or BLACK LIQUOR. —For use by calico-printers, a liquid consisting chiefly of a solution of ferrous acetate, but always containing more or less ferric acetate, is prepared by acting on scrap-iron by crude pyroligneous acid of 1·035 to 1·040 specific gravity. A purified acid gives less satisfactory results.[1] The product, which is a deep black liquid, has a density of 1·085 to 1·090, and is concentrated by boiling till the density is about 1·120, when it contains about 10 per cent. of iron. It is then ready for use, and is known as "printers' iron liquor." Much iron liquor is now made of a density as high as 1·140. For use by dyers, the liquid is not concentrated by evaporation, but the density is raised by the addition of ferrous sulphate (copperas), by which a more suitable product is said to be obtained than is yielded by acetate of iron alone. As a 5 per cent. solution of crystallised ferrous sulphate has a density of 1·026, the addition of ½ lb. of copperas to the gallon of "black liquor" will raise its density from 1·085 to 1·111. As much as 124 grammes of ferrous sulphate per litre has been met with in iron liquor. The sulphate

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[1] According to M. Moyret (*Jour. Soc. Dyers and* [*Colourists*, i. 117) the iron exists in black liquor both in the ferrous and ferric conditions, the intense colour and keeping qualities being due to the presence of a small quantity of pyrocatechol, $C_6H_4(OH)_2$, which is a constituent of pyroligneous acid and forms a black compound with ferroso-ferric oxide.

may also result from the addition of sulphuric acid to the pyroligneous acid employed for dissolving the scrap-iron. *Sulphate of iron* may be detected and estimated by precipitating the diluted black liquor with barium chloride. 233 parts of the precipitate represent 278 parts of crystallised ferrous sulphate. Black liquor is frequently adulterated with *common salt*, a 5 per cent. solution of which has a density of 1·036. It may be detected and estimated by adding nitric acid and precipitating the diluted liquor with nitrate of silver. *Chloride of iron* may also be present owing to the addition of hydrochloric to the pyroligneous acid. Hence the chlorine must not be assumed to exist as common salt without further examination. This is best effected by heating the liquid with nitric acid, adding barium nitrate to separate the sulphates, precipitating the iron and excess of barium by ammonia and ammonium carbonate, evaporating the filtrate to dryness, and igniting the residue, when any common salt will remain. *Tannin* is stated to be added to iron liquor.

FERROUS ACETATE is sometimes made by decomposing a solution of ferrous sulphate by calcium acetate. The liquor has usually a density of 1·11, and contains calcium sulphate.

FERRIC ACETATE is sometimes preferred by dyers and printers to the ferrous salt. It is occasionally prepared by decomposing iron-alum or ferric sulphate by lead acetate. The product must be free from excess of the lead salt, and, for some purposes, excess of ferric sulphate must be avoided.

Tincture of Acetate of Iron is used in medicine. It is prepared by mixing alcoholic solutions of potassium acetate and ferric sulphate, and filtering from the precipitated sulphate of potassium.

Lead Acetates.—These important salts include the neutral acetate, $Pb''(C_2H_3O_2)_2$, often called "sugar of lead," and no fewer than four basic- or oxy-acetates, all of which are more or less soluble in water, the solutions possessing an alkaline reaction and giving a precipitate of lead carbonate by the action of carbonic acid gas.[1] All the basic acetates may be considered as compounds of the neutral acetate with oxide or hydrate of lead. By suspending the substance in water, and passing carbonic acid through the liquid as long as it has an alkaline reaction, the lead oxide is separated as an insoluble carbonate, and may be filtered off, washed, ignited in porcelain (apart from the filter) till bright yellow when cold, and weighed as PbO. The lead remaining in permanent solution exists as *neutral acetate*, and may be determined by precipitation as sulphate or chromate.

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[1] A solution of neutral lead acetate is slightly precipitated by carbonic acid.

A better and simpler method for detecting basic acetate in a sample is to dissolve it in recently-boiled water, filter, and then add to the clear solution an equal measure of a 1 per cent. solution of mercuric chloride. A white precipitate proves the presence of basic acetate.[1] The assay may also be conducted by method *d*, *e*, or *h* of paragraph 889.

R. Fresenius recommends the following indirect method for the assay of pyrolignite and acetate of lead:—10 grammes of the sample are dissolved in water in a flask holding 500 c.c., 60 c.c. of normal sulphuric acid are added, and then water up to the mark. An extra 1·3 c.c. of water is added to compensate for the bulk of the precipitated lead sulphate. The flask is closed, well shaken, and the liquid allowed to settle. 100 c.c. of the clear liquid are taken out, precipitated with barium chloride, and the resultant $BaSO_4$ collected, washed, ignited, and weighed. Its weight, multiplied by ·4206, is subtracted from ·588 grammes (the weight of H_2SO_4 added to each 100 c.c. of the liquid). The remainder, multiplied by 113·7, gives the percentage of PbO in the sample. Another 100 c.c. of the clear liquid are drawn off and titrated with normal soda solution, using litmus as an indicator. Multiply the number of c.c. of alkali used by ·060, subtract from this the previously obtained weight of $BaSO_4$ multiplied by ·515 (=the free sulphuric acid expressed in terms of acetic acid), and the remainder, multiplied by 50, will be the percentage of acetic acid ($C_2H_4O_2$) in the sample.

Solution of Oxy-Acetate of Lead is an official remedy. It is described in the British Pharmacopœia as a colourless liquid of 1·26 specific gravity, alkaline reaction and sweet astringent taste; becoming turbid on exposure to air; and forming, with mucilage of gum arabic, a white opaque jelly. A dilute solution is officially prepared by mixing the above with an equal measure of alcohol, and then adding enough water to make up 80 times the original measure. Solution of oxy-acetate of lead is prepared by boiling 10 parts of neutral acetate with 7 of finely-powdered litharge and 40 of water. After boiling for half an hour, the liquid is filtered and made up to the original bulk with water (see footnote on p. 201).

Cupric Acetates.—Several of these salts are known and extensively used in the arts. They are prepared by the action of acetic acid on oxide or carbonate of copper, or upon metallic copper with access of air. The neutral acetate is freely soluble in water, but several basic acetates exist. They are of various shades of colour, and constitute the bodies known as blue and green verdigris.

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[1] Besides their reactions with mercuric chloride, carbonic acid, and litmus, the basic acetates of lead are distinguished from the neutral acetate by their property of being precipitated by a strong solution of nitre added in excess. The precipitate appears to be an ortho-nitrate of lead, $Pb_3''(NO_4)'''_2$.

Verdigris of good quality is dry, soluble in dilute acetic or sulphuric acid, and also in ammonia. Verdigris should not contain more than 4 per cent. of impurities. A good sample has the following percentage composition :—cupric oxide, 43·5 ; acetic anhydride, 29·3 ; water, 25·2 ; and impurities, 2·0.

Verdigris is frequently adulterated. Sand, clay, pumice, and chalk ; sulphates of barium, calcium, and copper ; and salts of iron and zinc are sometimes present. The presence of zinc in verdigris is due to the use of sheets of brass instead of copper for corrosion by acetic acid.

On dissolving the sample in dilute hydrochloric acid, any *sand, clay, pumice,* or *sulphate of barium* will be left insoluble, and may be collected and weighed. (About 3 per cent. of insoluble matter is allowable in verdigris. If the residue amount to 6 per cent. the sample is inferior. *Sulphate of calcium,* if present in large proportion, may be left partially in the insoluble residue.) If the sample effervesced on addition of acid, a *carbonate* is present, though it may be that of copper. From a measured portion of the solution in acid the *sulphates* may be precipitated by barium chloride, and the $BaSO_4$ collected and weighed.

For the detection of the *metals,* the sample should be ignited, the residue dissolved in hydrochloric acid, and the copper precipitated from the diluted liquid by a current of sulphuretted hydrogen. In the filtrate, the excess of sulphuretted hydrogen is destroyed by bromine water, the liquid nearly neutralised by ammonia, and then boiled with ammonium acetate. The precipitate, when washed and ignited, leaves the *iron* as Fe_2O_3. The filtrate from the iron precipitate is treated with sulphuretted hydrogen, and any white sulphide of *zinc* filtered off, carefully roasted, and weighed as ZnO. From the filtrate, the calcium is precipitated by ammonium oxalate. The precipitate yields calcium carbonate on gentle ignition, the weight being equal to the *chalk* in the quantity of the sample taken. The calcium may be determined more readily, but less accurately, by dissolving the sample in hydrochloric acid, precipitating the iron by bromine and ammonia, and then at once treating the blue ammoniacal filtrate with ammonium oxalate. Of course, it does not follow that all the calcium found exists as chalk, unless sulphates are absent.

936. HOMOLOGUES OF ACETIC ACID. Lower Fatty Acids.

Acetic acid is the most important and best known of the homologous series called "the fatty acids." These acids have the general formula $C_nH_{2n}O_2$; $C_nH_{2n-1}O,OH$; or $C_nH_{2n+1}{\cdot}COOH$. The lower members of the series are volatile liquids closely resembling acetic acid. The higher members of the series are insoluble in water, not volatile without decomposition, and solid at ordinary temperatures. The fatty acid series is known incompletely up to an acid with 30 atoms of carbon, but the greater number of the members are of very limited importance, and the recognition of the majority of them by reagents is at present impossible.

937. The higher members of the fatty acid series are almost exclusively obtained by the saponification of the fixed oils, fats, and waxes, and hence such of them as require description will be conveniently considered in the section of this work treating of the products of saponification of such bodies. This article is therefore limited to a consideration of such of the lower members of the series as are sensibly volatile or soluble in water, and hence liable to occur under the same circumstances as acetic acid.

938. With the exception of the first three, all the members of the acetic series of acids are capable of isomeric modification. The number of such modifications capable of existing increases rapidly with the number of carbon atoms in the molecules, and many such bodies have been actually obtained. As far as is known, however, all the acids of the acetic series obtainable from natural sources are either the normal-primary acids or the iso-primary acids. Such secondary and tertiary acids as are known have been hitherto obtained solely by synthetical means, and their consideration lies beyond the scope of the present work.

939. The following table gives the names of the normal and iso-acids of the acetic series up to the member with seven carbon atoms. Above caproic acid the modifications have been very imperfectly differentiated. A table of the still higher members of the series will be given in the section on "Saponification."

From this table it will be observed that the boiling points of the normal fatty acids show a tolerably regular rise of 18° to 22° C. for each increment of CH_2 added to the formula. The iso-acid in each case boils at a lower temperature than the normal acid, and has also a lower density. The specific gravity and solubility of the fatty acids, as also the solubility of many of their metallic salts, decrease with an increase in the molecular weight. The ethers of the fatty acids similarly diminish in solubility and volatility with each increase in the number of carbon atoms.

Empirical Formula.	Name.	Constitutional Formula.	Boiling Point °C.	Specific Gravity at 0° C.	Solubility in Water.
CH_2O_2	Formic acid, . .	$H\cdot COOH$	100		Miscible in all proportions.
$C_2H_4O_2$	Acetic acid, . .	$CH_3\cdot COOH$	119		Do.
$C_3H_6O_2$	Propionic acid, . .	$CH_3\cdot CH_2\cdot COOH$	140	1·016	Do.
$C_4H_8O_2$	Normal butyric acid .	$CH_3\cdot(CH_2)_2\cdot COOH$	163 ...	·9817 ...	Do.
	Iso-butyric acid; or dimethacetic acid,	$CH(CH_3)_2\cdot COOH$	... 154	... ·9598	Soluble.
$C_5H_{10}O_2$	Normal pentoic or valeric acid, . .	$CH_3\cdot(CH_2)_3\cdot COOH$	185 ...	·9577 ...	Sparingly (1 in 30)
	Iso-pentoic acid; ordinary valeric acid; or iso-propacetic acid, .	$CH(CH_2)_2\cdot CH_2\cdot COOH$	... 175	... ·9536	Do.
$C_6H_{12}O_2$	Normal caproic acid,	$CH_3\cdot(CH_2)_4\cdot COOH$	205 ...	·9450 ...	Nearly insoluble.
	Iso-caproic acid, .	$CH(CH_3)_2\cdot(CH_2)_2\cdot COOH$	... 199	... ·9310	Do.
$C_7H_{14}O_2$	Normal œnanthylic acid, ...	$CH_3\cdot(CH_2)_5\cdot COOH$	224 ...	·9345 ...	Almost insoluble.
	Iso-œnanthylic acid, .	$CH(CH_3)_2\cdot(CH_2)_3\cdot COOH$	... 213	... ...	Do.

940. As a rule, the iso-acids present very close resemblances to the corresponding normal acids, their lower densities and boiling points and greater susceptibility to oxidation being the most tangible distinctions. In some cases, differences are observable in the solubility and crystallisability of the salts.

941. As a class, the lower member of the acetic acid series may be separated from most other organic acids (except lactic acid), by treating the aqueous solution with finely-ground oxide of lead, in quantity sufficient to render it slightly alkaline. On filtering, the lead salts of most organic acids will be left insoluble, while those of the acetic series will be found in the filtrate.

The separation of the lower acids of the acetic series from each other cannot usually be effected very readily or perfectly, the most satisfactory methods being based on the following principles :—

a. The lowest members of the series are the most readily soluble in aqueous liquids, formic, acetic, propionic, and normal butyric acid being soluble in all proportions. All but formic and acetic acids are separated from their aqueous solutions by saturating the liquid with calcium chloride, when they rise in the form of oils. A more perfect separation from acetic and formic acids of the acids higher than valeric may be effected by shaking the acidulated aqueous solution with ether, which dissolves the higher homologues together with more or less of the lower. On agitating the ethereal layer with a strong solution of calcium chloride the formic and acetic acid pass into the latter, and by repeating the treatment may be perfectly removed from the ether, with little or no loss of the higher homologues.

b. The lower members of the series are most chemically active Hence, if an amount of alkali insufficient for complete neutralisation be added to a solution containing the free acids, and the liquid be then distilled, the higher members of the series pass over in the free state, while the lower members remain behind as fixed salts.

Thus if caustic soda be added to a mixture of butyric and valeric acids in quantity insufficient to neutralise the whole, and the liquid be then distilled, the distillate will consist of pure valeric acid and the residue will contain mixed butyrate and valerate of sodium; or else the distillate will contain the whole of the valeric acid and some butyric acid, and the residue will consist entirely of butyrate of sodium. In either case, a portion of one of the acids is obtained free from the other. In the first case the residue of mixed valerate and butyrate of sodium may be treated with sufficient dilute sulphuric acid to neutralise one-half of the soda originally used, and the mixture redistilled, when a fresh quantity of valeric acid will be obtained, either pure or mixed with butyric acid according to the relative proportions of the two acids present in the original mixture. In the latter case, by partially neutralising the distillate with soda, and again distilling, a further separation may be effected, and by repeating the operation in a judicious manner two or even more of these volatile fatty acids may be separated tolerably perfectly from each other.

Although the foregoing method is well suited to the separation of normal butyric and valeric acids, the principle is wholly at fault when iso-valeric acid is in question, for this acid completely decomposes normal butyrates.

c. An approximate separation of the homologues higher than valeric acid can be effected by a fractional crystallisation of their barium salts. The following is the order in which the barium salts are deposited :[1]—

From Aqueous Solutions.	From Alcoholic Solutions.
1. Barium caprate.	1. Barium caprylate.
2. ,, pelargonate.	2. ,, œnanthylate.
3. ,, caprylate.	3. ,, pelargonate and caprate.
4. ,, œnanthylate.	4. ,, caproate.
5. ,, caproate.	

The aqueous or alcoholic solution of the acid is neutralised with standard aqueous or alcoholic solution of potash (according as the crystallisation is to be effected from an aqueous or alcoholic solution), an amount of barium chloride equivalent to the potash is next added, and the resultant liquid evaporated and allowed to deposit crystals. The crops of crystals from an aqueous solution may be washed with hot alcohol, the washings containing the salts in the reverse order of their deposition from alcoholic solution.

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[1] It is very probable that this method would be much affected by a change in the modifications of the acids. The normal and iso-varieties of the higher fatty acids are not at present thoroughly differentiated.

d. Another method of detecting and estimating acids of the acetic series when in admixture with each other is based on the different composition of their barium salts, the process being as follows:—The free acids obtained by distillation are saturated by carbonate of barium, or by the cautious addition of baryta water (using phenol-phthaleïn to indicate the point of neutrality),—the latter method being preferable for the higher numbers of the series. In this way, neutral barium salts are formed, which may be obtained in the anhydrous state by evaporating off the water and drying the residue at 130° C. These barium salts contain percentages of barium dependent on the atomic weights of the fatty acids present. On moistening the residue with sulphuric acid and then igniting, an amount of barium sulphate is obtained proportional to the percentage of barium contained in the salt of the fatty acid present. Instead of weighing the barium sulphate, a standard solution of baryta water may be employed and the weight of barium (or its equivalent of $BaSO_4$) calculated from the volume of solution employed. This method also serves as a useful check on the determination of the weight of barium sulphate. The following table shows the proportions of Ba contained in, and of $BaSO_4$ producible from, the barium salts of the lower acids of the acetic series:—

Name of Salt.	Formula of Salt.	Ba, per cent.	$BaSO_4$, per cent.
Barium formate, . .	$Ba,2CHO_2$	70·25	119·47
,, acetate, . .	$Ba,2C_2H_3O_2$	53·73	91·37
,, propionate, .	$Ba,2C_3H_5O_2$	48·41	82·13
,, butyrate, . .	$Ba,2C_4H_7O_2$	44·05	74·91
,, valerate, . .	$Ba,2C_5H_9O_2$	40·41	68·73
,, caproate, . .	$Ba,2C_6H_{11}O_2$	37·33	63·48
,, œnanthylate .	$Ba,2C_7H_{13}O_2$	34·68	58·98
,, caprylate, .	$Ba,2C_8H_{15}O_2$	32·39	55·08
,, pelargonate .	$Ba,2C_9H_{17}O_2$	30·38	51·66
,, caprate, . .	$Ba,2C_{10}H_{19}O_2$	28·60	48·64

From this table it will be seen that the pure barium salts of the lower acids of the acetic series can very readily be distinguished from each other by estimating the percentage of barium contained in them. In the case of mixtures of two acids the identity of which is established, the proportions in which the two are present may be calculated from the following formula, in which x is the percentage of barium salt of the lower fatty acid in the mixed barium salts obtained; P, the percentage of $BaSO_4$ yielded by the mixed barium salts on treatment with sulphuric acid; B, the percentage of $BaSO_4$ theoretically obtainable from the pure salt of the lower fatty acid; and b, the percentage of $BaSO_4$ theoretically obtainable from the pure salt of the higher fatty acid. Then:—

$$Bx = 100P + bx - 100b.$$

For example:—suppose a mixed barium salt known or assumed to consist of acetate and valerate to have yielded 78·45 per cent. of $BaSO_4$, when treated with sulphuric acid and ignited. Then, by the above formula,

$$91{\cdot}37x = 7845 + 68{\cdot}73x - 6873$$

therefore $$22{\cdot}64x = 972$$

and $$x = 42{\cdot}93\,.$$

Hence, the mixed barium salt consisted of 42·93 of barium acetate, and 57·07 of barium valerate. From these data, and the weight of mixed barium salt found, the actual amounts of acetic and valeric acid may be readily calculated.

The above method has been proposed by A. Dupré (*Analyst*, i. 4) for approximately determining the fusel oil in spirits. In this case the various alcohols are first converted into the corresponding acids by oxidation with chromic acid mixture (see par. 273).

e. A most ingenious method of detecting other fatty acids in presence of acetic acid, and estimating the proportions present, has been described by M. Duclaux (*Ann. Chem. Phys.* [5] ii. 233). It is based primarily on the curious fact that if a liquid containing any fatty acid be distilled, each successive fraction of the distillate contains a proportion of the total acid operated on which is practically constant for the same fraction, but will vary according to the nature of the acid employed. Thus M. Duclaux found that if 110 c.c. of a liquid containing acetic acid were distilled in a retort of 250 to 300 c.c. capacity, each succeeding 10 c.c. of distillate contained an increasing quantity of acid, which amounted to 79·8 per cent. of the whole when 100 c.c. had passed over. Each of the homologues of acetic acid has a special rate of vaporisation, and it is a curious fact that the less volatile acids pass over with the first portions of aqueous vapour, while acetic and formic acids behave in an opposite manner.[1]

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[1] The following table gives M. Duclaux's results in a concise form. The columns headed "B." show the percentages of the total acid contained in each

The presence of foreign matters has a sensible, but not very serious effect on the rate of distillation. Alcohol diminishes the

successive 10 c.c. of distillate, when 110 c.c. of the liquid were distilled in a retort holding 250 to 300 c.c. The columns headed "A." show the percentages of the total distilled acid which passed over in each 10 c.c. when the 100 c.c. first obtained was redistilled. The determinations of acid in the distillate were made by standard lime water:—

	Percentage of Total Acid contained.									
	Formic.		Acetic.		Propionic.		Butyric.		Valeric.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1st fraction of 10 c.c. .	5·5	3·5	7·5	5·9	11·3	10·5	16·8	16·4	Not determined.	24·5
2nd " " .	6·4	4·1	7·9	6·2	11·5	10·6	15·1	14·7		20·0
3rd " " .	6·6	4·2	8·2	6·7	11·2	10·4	13·5	13·2		15·4
4th " " .	7·2	4·5	8·6	6·9	10·6	9·9	12·3	11·8		11·4
5th " " .	8·3	5·3	9·1	7·3	10·7	9·9	10·2	10·1		8·2
6th " " .	9·1	5·7	9·6	7·6	10·1	9·3	9·3	9·1		6·2
7th " " .	10·0	6·4	10·2	8·2	9·3	8·9	7·8	7·6		4·0
8th " " .	12·1	6·7	11·5	9·2	9·3	8·5	6·4	6·3		3·1
9th " " .	14·6	9·3	12·4	9·8	8·5	7·8	5·0	4·8		2·6
10th " " .	20·2	12·8	15·1	12·1	7·5	7·0	3·6	3·5		1·5
Total distillate = 100 c.c.	100·0	63·5	100·0	79·8	100·0	92·8	100·0	97·5		96·9
Remaining in retort = 10 c.c.	...	36·5	...	20·2	...	7·2	...	2·5		3·1

It appears from this table that when a solution of acetic or formic acid is distilled, the first portions which come over are very weak, and that the strength of the distillate rises regularly till the end of the operation. On the other hand, propionic, butyric, and valeric acids come over chiefly at the commencement of the process.

When two or more of these acids are present together in a liquid, each maintains its own characteristics when the distillation is carried out as described. Hence, not merely the nature but the quantities of the acids present may be ascertained by calculation—at least in certain cases. Thus, suppose the numbers obtained for the "B" column by the distillation of a certain liquid to have been as follow:—8·6, 8·7, 8·7, 8·7, 8·8, 8·7, 8·9, 9·1, 9·7, 10·3 per cent. These results may safely be presumed to be produced by a mixture of acetic acid with either butyric or propionic acid. Assume the mixture to consist of *a* equivalents of acetic and *p* equivalents of propionic acid; then, by the table, we have for the 1st fraction of 10 c.c.—

$$8{\cdot}6(a+p)=5{\cdot}9a+10{\cdot}5p$$
$$\therefore\ p=1{\cdot}2a.$$

Proceeding in the same way with the percentages of acid found in the succeeding fractions of distillate, we obtain the following series of numbers:—1·1, 1·0, 1·0, 1·0, 1·0, 1·0, 1·0, 1·0, 1·1. Hence the amount of propionic acid is the same, or slightly in excess, in equivalents, of the acetic. For various proportion of acid in the first portions of the distillate, but by the time $\frac{10}{11}$ths has distilled the proportion of acid in the receiver is

reasons, the inferences to be drawn from the first and last fractions are the least trustworthy. But suppose the mixture were one of acetic and butyric acids ; then,

$$8{\cdot}6(a+b) = 5{\cdot}9a + 16{\cdot}4b$$
$$\therefore\ b = 3{\cdot}2.$$

Proceeding similarly with the other fractions, we obtain the following series of numbers :—3·1, 3·0, 2·8, 2·5, 2·5, 2·2, 2·1, 1·6, 1·3. Thus we have ten estimations of the butyric acid, in which its equivalent amount varies from 3·2 to 1·3 times the acetic acid present. The variation in these determinations renders the assumption of the second acid being butyric acid absurd. Hence, the two acids were acetic and propionic in about equivalent proportions.

In the original paper, M. Duclaux gives a number of tables which materially facilitate calculation.

In applying the method to the examination of wines, Duclaux recommends the following mode of procedure :—

275 c.c. ($= 25 \times 11$), or a multiple of this quantity are shaken, and a current of air passed through the liquid, in order to remove carbon dioxide. The wine is then distilled till 250 c.c. have passed over, and the distillate, after again drawing air through it, is titrated with standard lime water. An excess of the latter is then added, and the liquid is evaporated to about 250 c.c. in order to volatilise the alcohol. A gramme of glycerin is then added, and sufficient tartaric acid to set all the volatile acids at liberty. The calcium tartrate is allowed to crystallise, and is then separated from the liquor, the volume of which is again brought to 275 c.c. About 1 gramme of tartaric acid is now added, and the liquid distilled till 250 c.c. have passed over, when the whole distillate is again titrated. The lime water now required will bear the same proportion to that used for the first titration, that the amount of volatile acid indicated by the first titration bears to the total quantity present in the wine. The titrated liquid is now brought to 165 c.c., and 150 c.c. distilled over, after adding an amount of tartaric acid exactly equivalent to the lime water used in the titration. 50 c.c. of the distillate are titrated, while the remainder is diluted to 110 c.c., and 100 c.c. distilled over each fraction of 10 c.c. being separately titrated. The numbers thus obtained give the necessary data for ascertaining the nature and amount of the volatile acids present.

The following example indicates the mode of calculation:—275 c.c. of wine were taken and distilled to $\frac{1}{11}$. 250 c.c. of distillate required 316 c.c. of lime water. On adding tartaric acid and distilling over $\frac{10}{11}$, the distillate required 263 c.c. of lime water. Hence 83·3 per cent. of the total acid passed over on distilling to $\frac{1}{11}$, and, assuming the same proportion in the first distillation, the free acid in the original wine would have required $\frac{316}{263}$ of $316 = 379$ c.c. of lime water for its neutralisation. On referring to the table on page 409, it will be seen that, when a liquid containing acetic acid is distilled to $\frac{1}{11}$ of its bulk, about 80 per cent. of the acid passes over, while 93 per cent. of the propionic the same as in the absence of alcohol. Glycerin diminishes slightly the proportion of acid volatilised, doubtless owing to the formation of a glycylic ether, but the effect can be destroyed by adding tartaric acid to the contents of the retort.

The writer has no personal experience of Duclaux's process, beyond an attempt to apply it to the assay of commercial "acetate of lime." The salt was dissolved in water, oxalic acid added, and the calcium oxalate filtered off. On distilling the filtrate to $\frac{1}{11}$, a tolerably constant proportion of acetic acid passed over, but it was considerably below 79·8 per cent. of the total quantity present in the sample.

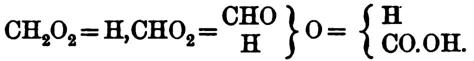
acid distils under similar circumstances. On repeating the process, 80 and 93 per cent. of *these* amounts will be respectively obtained. Hence the third and last distillate will contain $\frac{80 \times 80 \times 80}{100 \times 100 \times 100} = \frac{512}{1000} = 51{\cdot}2$ per cent. of the total acetic acid present in the wine, and $\frac{93 \times 93 \times 93}{100 \times 100 \times 100} = 80{\cdot}4$ per cent. of the total propionic acid. Thus if the titration of the fractions obtained in the third distillation showed acetic and propionic acid to be present in equivalent proportions, the equivalent amounts of these acids present in the original wine would be as 804 to 512, or as 100 equivalents of acetic to 63·7 of propionic acid. Thus of 379 c.c. of lime water, required by the volatile acids in 275 c.c. of the original wine, $\frac{100}{164}$ of that quantity, or 231 c.c., were neutralised by acetic acid, and the remaining 148 c.c. by propionic acid. From the strength of the lime water and the atomic weights of acetic and propionic acids, the actual amounts of fatty acids present can be readily calculated.

By this method, Duclaux proved the presence of valeric acid in perspiration and of butyric acid in bread. He also found that the presence of butyric acid was characteristic of wine suffering from "bitterness," and propionic acid of wine in which the fermentation had been "pushed" too far.

The largest quantity of valeric acid found in wine by Duclaux was ·006 grammes per litre. For its discovery, 7 or 8 litres must be distilled as already described, the distillate neutralised with lime, and then $\frac{1}{40}$ of the sulphuric acid necessary to decompose the calcium salts added. On redistillation, the whole of the valeric acid passes over, while 39 equivalents out of every 40 of the fatty acids present remain in the retort.

In Duclaux's process, standard baryta water might probably be advantageously substituted for the lime water, and standard sulphuric acid for the tartaric acid recommended (except where about 1 gramme of tartaric acid is directed to be added to represent the acidity of the original wine). This modification would allow the sulphate of barium to be filtered off immediately instead of having to wait for the calcium tartrate to crystallise. In the last titrations, the use of baryta water would cause the acids to be obtained in the form of barium salts, which could be dried at 130° C., weighed, and converted into $BaSO_4$, as described in method *d*, page 407. A very useful check would thus be obtained.

942. Formic Acid.



$$\mathrm{CH_2O_2 = H,CHO_2} = \left.\begin{matrix}\mathrm{CHO}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O} = \left\{\begin{matrix}\mathrm{H}\\ \mathrm{CO.OH.}\end{matrix}\right.$$

Formic acid is contained in the liquid obtained by distilling ants with water. The stings of bees and wasps, as also of stinging nettles and hairy caterpillars, owe their irritating power to formic acid. It is usually prepared by distilling oxalic acid with glycerin. It also results from the decomposition of chloroform or chloral by an alkali, by the reaction of carbon monoxide and caustic alkalies, and by the reaction of cyanogen gas or cyanides with water, besides numerous other reactions.

943. Formic acid is a colourless volatile liquid, of extremely irritating pungent odour. Absolute formic acid has a density of 1·2211 at 20° C., and boils at 100°. Formic acid has a penetrating smell, and purely acid taste. When concentrated, it produces intense irritation on the skin.

In general properties, formic acid strongly resembles acetic acid, but it is stronger in its chemical affinities, and more readily oxidised.

944. The *formates* mostly crystallise well and are all soluble in water. Heated with concentrated sulphuric acid they do not blacken, but evolve pure carbon monoxide, as an inflammable gas burning with a blue flame. A neutral solution of a formate of alkali-metal gives the following reactions :—

a. Nitrate of silver gives, in concentrated solutions, white crystalline argentic formate, $AgCHO_2$, which darkens on standing, and is reduced to metallic silver when warmed. If the liquid be too dilute to allow of a precipitate being formed, the reduction to metallic silver still occurs on heating, a mirror being frequently formed on the sides of the tube. In presence of ammonia the reduction is retarded or prevented.

b. Mercuric chloride is reduced on heating, with production of white mercurous chloride, or grey metallic mercury, according to the proportion of formate present. Acetates do not give this reaction, but acetates and chlorides of alkali-metals retard or prevent the reduction. The reduction of formate of mercury on heating may be applied to the estimation of formic acid, and its separation from acetic acid may be approximately effected by boiling the solution of the free acids with *yellow* mercuric oxide until effervescence ceases. If formic acid only be present, the filtered liquid will be free from mercury. With a mixture of the two acids, the amount of mercury which passes into solution is equivalent to the acetic acid present. If the total acid present originally be determined by standard alkali or other means, the quantity of formic acid may be found. Or, in presence of other acids forming soluble mercuric salts, the excess of mercuric oxide may be dissolved by dilute hydrochloric acid, and the residual metallic mercury weighed and calculated to formic acid. $HgO + CH_2O_2 = Hg + CO_2 + H_2O$.

c. Chlorine, bromine, chromic acid, permanganate, and other powerful oxidising agents convert formic acid more or less readily into carbonic acid.

d. When heated gently with alcohol and sulphuric acid, formates generate ethyl formate, C_2H_5,CHO_2, having a fragrant odour of peach-kernels, and boiling, when purified, at 54°·4 C.

e. With ferric chloride, formates react similarly to acetates (see test *e*, par. 888).

f. At a gentle heat, strong sulphuric acid evolves carbon monoxide from formic acid or a formate. Strong alkalies produce an oxalate.

g. Formates of lead and magnesium are insoluble in alcohol, while the corresponding acetates are soluble. Hence, acetic may be separated from formic acid by saturating the free acids with a slight excess of calcined magnesia or carbonate of lead, filtering, evaporating the filtrate to a small bulk, and adding a large proportion of alcohol. Formate of magnesium or lead is precipitated, while the corresponding acetate remains in solution. The process may be varied by precipitating the alcoholic solution of the acids with an alcoholic solution of lead acetate, and washing the resultant precipitate with alcohol.

945. In addition to the methods already indicated, formic acid may be *determined* by titration with standard alkali, or by decomposition in a carbonic acid apparatus by sulphuric acid and bichromate of potassium, the amount of formic acid present being deduced from the weight of dry CO_2 evolved. $CH_2O_2 + O = H_2O + CO_2$.

946. Propionic Acid.

$$C_3H_6O_2 = H,C_3H_5O_2 = \left.\begin{matrix} C_3H_5O \\ H \end{matrix}\right\} O = \left\{\begin{matrix} C_2H_5 \\ CO.OH. \end{matrix}\right.$$

This body, formerly called metacetonic acid, is of no commercial importance, but its detection and separation from its homologues are occasionally necessary.

Propionic acid is contained in crude oil of amber, in sour cocoanut milk, and in certain wines, especially when the fermentation has been pushed too far. It is also produced by the fermentation of glycerin, lactic acid, &c., and by a great variety of synthetical methods.

947. Propionic acid closely resembles acetic acid, but has an odour recalling at once those of acetic and butyric acids. It boils at 140°, and has a density of ·996 at 19°.

The statements respecting the solubility of propionic acid are very conflicting. According to some observers it is not miscible in all proportions with water, but floats as an oil on its saturated aqueous solution; according to others, it is not separated from its aqueous solution by a saturated solution of calcium chloride. Both these statements are probably incorrect.

The *propionates* closely resemble the acetates; they are all soluble in water.

948. The following method is described by Linnemann for the separation of propionic acid from its lower homologues:—The free acids are evaporated to dryness with excess of litharge. The residue is then treated with cold water, and the liquid filtered. Basic propionate of lead dissolves, while any acrylate remains insoluble, together with most of the acetate and formate. The solution is boiled and stirred quickly, when the propionate separates suddenly and almost completely as a crystalline precipitate, soluble in cold water, but which may be filtered at a boiling heat from the remaining acetate and formate. The propionic acid of fermentation is said not to exhibit this reaction.

For other methods of detecting and separating propionic acid, see process *e*, par. 941.

949. Butyric Acid.

$$C_4H_8O_2 = H,C_4H_7O_2 = \left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O.$$

Two isomeric modifications of this acid are known, differing slightly in their physical properties (see par. 939).

950. *a.* NORMAL BUTYRIC ACID, $C_3H_7{\cdot}COOH$, occurs ready-formed in various natural products, and is frequently produced by the decomposition of animal and vegetable matter. It exists as a glyceride in butter and cod-liver oil and results from the butyric fermentation of sugar.

Normal butyric acid is a colourless mobile liquid, having a smell at once resembling acetic acid and rancid butter. It is soluble in water, alcohol, and ether in all proportions, but is not soluble in concentrated solution of calcium chloride or common salt; hence, it may be separated from its aqueous solution by saturating the liquid with calcium chloride, and then agitating with ether. From the ethereal layer it may be recovered by spontaneous evaporation, or, as a salt, by agitation with excess of solution of potash or soda.

For other methods of approximately separating butyric from acetic and valeric acids see par. 941.

951. *β.* ISO-BUTYRIC ACID, $CH(CH_3)_2{\cdot}COOH$, occurs in carob beans, and among the acids of castor oil. It closely resembles the normal acid in its general properties, but has a lower boiling point

and density. Its smell is less offensive than that of the normal acid obtained by the decomposition of butter, or by the butyric fermentation of sugar. It requires three parts of cold water for solution, and is easily oxidised to acetic acid and carbon dioxide when heated with chromic acid mixture (par. 295).

952. All the metallic *butyrates* are soluble in water. Butyrate of lead is a heavy liquid, which solidifies when cooled.

Butyrate of copper forms bluish-green monoclinic crystals, which are sparingly soluble in water. The formation of cupric butyrate may be employed to distinguish butyric from valeric acid. (See p. 417.)

953. The *iso-butyrates* closely resemble the butyrates, except in the cases of the calcium and silver salts. *Normal butyrate of calcium* is very soluble in cold water, but separates as a crystalline precipitate on heating the strong solution to 70°. The *iso-butyrate* is more soluble in hot water, and separates on cooling as a crystalline magma.

954. The most delicate and characteristic reaction of butyric acid or a butyrate is the formation of ethyl butyrate on heating with alcohol and strong sulphuric acid. The ether has a most fragrant odour of pine-apple, and boils at 120° C. (See par. 290.)

955. Pentoic Acid. Valeric Acid.

$$C_5H_{10}O_2 = H,C_5H_9O_2 = \left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O.$$

Several acids of this formula are known, namely,—

956. α. PRIMARY NORMAL PENTOIC ACID, $CH_3{\cdot}(CH_2)_3{\cdot}COOH$; boiling at 185°C., and having a density of ·9415 at 20°, is obtained, together with paraffins and normal homologous acids, when fats are distilled with superheated steam; also by the action of alkalies on normal butyl cyanide. The smell resembles that of normal butyric acid. The *calcium* salt has a fatty lustre and crystallises in scales, more soluble in cold than in hot water.

957. β. PRIMARY ISO-PENTOIC ACID, or ordinary Valeric Acid, $CH(CH_3)_2{\cdot}CH_2{\cdot}COOH$, occurs in dolphin and porpoise oils, in sweat, and in various other products and secretions of animals. It exists ready-formed in valerian-root, and many plants of the natural order *Compositæ*. It may be obtained by the oxidation of the iso-amyl alcohol of fusel oil (par. 266); or by the action of alkalies on iso-butyl cyanide. Iso-valeric acid is frequently called simply "valeric acid," though the name valerianic acid would serve better to indicate its origin, and thereby distinguish it from other modifications of pentoic acid.

Valerianic Acid is an optically inactive and colourless oily liquid, having an unpleasant smell resembling old cheese. Its taste is sharp and acid, and it blanches the tongue. Valerianic acid dissolves in about 30 parts of cold water, and is readily soluble in alcohol, ether, chloroform, or strong acetic acid. It is almost wholly removed from its aqueous solution by saturating the liquid with common salt or calcium chloride.

Absolute valerianic acid has a density of ·937 at 15°, and boils at 175° C. It forms a hydrate of the composition $C_5H_{10}O_2,H_2O$, having a density of ·950 and boiling at 165°, but it is gradually dehydrated by distillation, the weaker acid coming off first. On the other hand, on distilling dilute aqueous valerianic acid, the first portions of the distillate are most strongly acid. (See par. 941, *e.*)

958. γ. SECONDARY PENTOIC ACID. Active Valeric Acid. Methyl-ethyl-acetic acid, $CH(CH_3)(C_2H_5){\cdot}COOH$. This acid resembles ordinary valeric acid, but boils at 172° C. (3 degrees lower), and is easily oxidised by chromic acid mixture (par. 295) into acetic acid, carbon dioxide, and water. It is obtained by the oxidation of the lævo-rotatory amyl alcohol of fusel oil, but the acid itself is *dextro*-rotatory. It also differs from ordinary valeric acid in forming a very soluble barium salt, the solution of which dries up to an amorphous varnish.

959. δ. TERTIARY PENTOIC ACID, or Trimethyl-acetic Acid, $C(CH_3)_3{\cdot}COOH$, is solid at ordinary temperatures, melting at 35°·4 to a liquid of ·905 specific gravity at 50°, and boiling at 163°·8.

960. REACTIONS OF ISO-VALERIC ACID AND ISO-VALERATES.

When iso-valeric acid or an iso-valerate is distilled with sulphuric acid and a little amylic alcohol, a fragrant ethereal liquid smelling of apples is obtained; this is the iso-valerate of amyl (par. 290).

Iso-valerates are decomposed by acetic acid with formation of iso-valeric acid and an acetate; they are also decomposed by tartaric, citric, and malic acid. Some observers state that they are decomposed by butyric acid, and others deny this.

Metallic *iso-valerates* are mostly soluble in water. The oxy-valerates of iron and bismuth are insoluble. Argentic and mercurous valerates are but slightly soluble, and valerate of aluminium is insoluble. Nether valerianic nor butyric acid gives a precipitate with an aqueous solution of zinc acetate. This fact distinguishes them from *caproic acid*, which throws down sparingly soluble zinc caproate as a white crystalline precipitate.

Iso-valerate of barium crystallises easily in triclinic scales or tables (in distinction from active valeric acid), is soluble in two parts of cold water, and sparingly soluble in alcohol. *Caprylate* of barium requires 120 parts of cold water for solution, and is nearly insoluble in alcohol. *Caprate* of barium is almost insoluble in water.

When concentrated valerianic acid is agitated with solution of cupric acetate, anhydrous cupric iso-valerate separates in oily droplets, which, in from five to twenty minutes, crystallise as greenish-blue monoclinic prisms or octohedra of hydrated cupric iso-valerate, moderately soluble in water and alcohol. The salt is less soluble in hot water than in cold, and hence the saturated solution becomes turbid when heated. This reaction distinguishes valeric from butyric acid, which forms with a moderately strong solution of cupric acetate an *immediate* precipitate or turbidity of cupric butyrate, of bluish-green colour, and crystallising in small monoclinic prisms. In using this test for assaying valerates, the acid must first be obtained free by distilling the salt with a moderate excess of sulphuric acid.

Valeric acid may be separated from most organic acids by converting it into the soluble valerate of lead. Acetic acid may be detected by neutralising any free acid with soda, and precipitating in the cold with excess of ferric chloride. In presence of acetic or formic acid, the filtered liquid will have a red colour. The insolubility of aluminium valerate might probably be employed for the separation of valeric from acetic or formic acid.

For other methods of approximately determining valeric acid and separating it from its homologues, see par. 926.

961. Commercial Valerianic Acid and Valerianates.

The presence of *alcohol*, *acetic acid*, *butyric acid*, *valerates*, &c., in commercial valerianic acid is indicated by the increased solubility of the sample, which should not be greater than 1 of the hydrated acid in 26 parts by weight of water. If the sample require more than 30 parts of cold water for solution, the presence of *higher homologues*, or *valeral* (valeric aldehyde, $C_5H_{10}O$) is indicated. Acetic acid may be recognised as indicated in par. 959. By neutralising the sample with an alkali, any *amylic alcohol*, valeric aldehyde, or *neutral ethers* will be left undissolved, as a turbidity or oily layer, and the amount may be estimated by measurement, or the mixture may be shaken with ether, and the ethereal liquid evaporated spontaneously. The solubility of valeric acid in a mixture of equal volumes of glacial acetic acid and water may be employed to separate it from valeral and ethers, but not from amylic alcohol.[1] The presence of butyric acid will be indicated by fractional distillation, and by the composition of the salt obtained by saturating the acid with carbonate of barium (see par. 926, *d*); also by the reaction with cupric acetate (par. 959).

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[1] Valeric acid may be purified by dissolving in two equivalents of the crude acid one of neutral valerate of sodium, assisting the solution by a gentle heat. On standing in a cool place, crystals of an acid valerate of sodium are deposited, and on distilling this with sulphuric acid, and collecting the liquid which passes over between 125° and 138°, pure valeric acid is obtained.—*Lescœur.*

Valeric acid should also be tested for non-volatile impurities, sulphuric acid, and hydrochloric acid.

Valerianates have been somewhat extensively used in medicine, especially the sodium, iron, zinc, and bismuth salts. They are all more or less liable to sophistication, which in some instances is of a very gross kind. Thus, samples of "valerianate of zinc" are occasionally composed of the sulphate or acetate, and others have been met with which consisted of butyrate of zinc impregnated with oil of valerian. Valerianate of zinc is also liable to adulteration with tartaric and citric acids, boric acid, and salts of the light metals. Similarly, tartrate or citrate of iron flavoured with valerian has been substituted for the valerate of iron, and the sulphate of quinine for the valerate. "Valerianate of ammonium" has been prepared by saturating chloride of calcium with oil of valerian, and many similar frauds have been occasionally practised.

Most of the above adulterations may be readily detected. The substitution of butyrate of zinc for the valerate is best recognised by distilling the salt with sulphuric acid diluted with an equal measure of water, and then applying the cupric acetate and other tests to the distillate.

The most satisfactory ready test for valerates is to weigh or measure the layer of free acid which separates on decomposing the solid salt with sulphuric acid diluted with an equal measure of a saturated aqueous solution of sulphate of zinc.

962. LACTIC ACID.

French—Acide Lactique. *German*—Milchsäure.

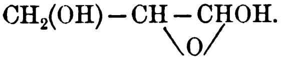
$$C_3H_6O_3 = H,C_3H_5O_3 = \left.\begin{matrix} C_3H_5O_2 \\ H \end{matrix}\right\} O.$$

Three modifications of lactic acid are known, namely:—

a. ORDINARY, or ETHYLIDENE-LACTIC ACID, $CH_3-CH(OH)-CO{\cdot}OH$. This acid results from a peculiar fermentation of saccharine matter, and is produced in a great variety of reactions. It is present in sour milk, and is probably the principal free acid of sour beer.

b. PARA-, SARCO-, or ETHYLENE-LACTIC ACID, $CH_2(OH)-CH_2-CO{\cdot}OH$, exists in the juice of lean meat; and

c. HYDRACRYLIC ACID, having probably the constitution



$$CH_2(OH)-\underbrace{CH-CH}_{O}OH.$$

963. The differences between *ordinary* and *paralactic acid* are most observable in their calcium and zinc salts. (See par. 968 *et seq.*) The free acids are hardly distinguishable, except that paralactic

acid is dextro-rotatory while ordinary lactic acid is inactive. Ordinary lactic acid forms a deep-blue liquid with cupric sulphate, while paralactic acid is almost completely precipitated. They also differ in their products of oxidation, paralactic acid yielding malonic acid, $C_3H_4O_4$, while ordinary lactic acid is converted into aldehyde or acetic acid, and carbonic or formic acid (see par. 950). By hot nitric acid, lactic acid is converted into oxalic acid.

Hydracrylic Acid is distinguished from its two isomers by the fact that it yields no trace of lactide when heated, but is resolved, almost without residue, into water and acrylic acid. $C_3H_6O_3 = H_2O + C_3H_4O_2$. Hydracrylic acid is more readily oxidised than the other varieties of lactic acid, giving off formic and much carbonic acid.

964. *Concentrated lactic acid* is a colourless, odourless, syrupy liquid, of a very acid taste. The specific gravity of the pure acid is said to be 1·248, and of that containing 75 per cent., 1·212;[1] but it is very doubtful whether the absolute acid has ever been obtained, owing to its tendency to form anhydrides. Lactic acid is not volatile without decomposition. At 130° C. it begins to decompose, and at about 145° C. sparingly soluble dilactic acid, $C_6H_{10}O_5$, is formed, which, at a higher temperature, forms volatile lactide or lactic anhydride, $C_3H_4O_2$, and other products.

Dilactic acid and lactide are nearly insoluble, but are converted by prolonged boiling with water, and readily by solutions of caustic alkalies, into lactic acid. The lactide obtained by heating paralactic acid yields ordinary lactic acid when treated in this manner.

In its ordinary metallic salts, lactic acid is monobasic, but a second atom of hydrogen can be replaced by alcohol-radicles.

Lactic acid is miscible in all proportions with water, alcohol, glycerin, and ether. It is but slightly soluble in chloroform, and is insoluble in carbon disulphide and petroleum spirit. Glyceric acid, $C_3H_6O_4$, which resembles lactic acid, is insoluble in ether.

Lactic acid dissolves recently precipitated phosphate of calcium, and is frequently used for that purpose.

965. Concentrated sulphuric acid mixes with pure lactic acid without blackening it. On heating, a brown colour is developed, and much carbon monoxide evolved, a brown humus-like body being ultimately left.

Lactic acid does not reduce Fehling's solution, but rapidly decolorises permanganate, both in acid and in alkaline solutions with production of an odour of aldehyde. Lactate of silver is imperfectly reduced on boiling, with production of a blue liquid and a brownish deposit.

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[1] According to Hager, a density of 1·212 corresponds to 80 per cent. of absolute lactic acid.

Lactic acid may be separated from organic acids forming insoluble lead salts by precipitating the solution (previously neutralised if necessary) with acetate of lead, either with or without an addition of alcohol. Lead lactate remains in solution, and may be decomposed by sulphuretted hydrogen, when free lactic acid is obtained.

Many admixtures may be got rid of by saturating the free acid by barium carbonate. When the aqueous solution is evaporated, and the residue treated with alcohol, many of the acids whose barium salts are soluble in water remain behind, whereas barium lactate dissolves in alcohol. Free lactic acid may be obtained by cautiously precipitating the solution of barium lactate with dilute sulphuric acid, and filtering.

When purified from all substances except those soluble in alcohol, the aqueous liquid containing free lactic acid may be saturated with oxide of zinc, evaporated to dryness, and the residue digested with alcohol. Lactate of zinc, insoluble in alcohol, remains, while the other matters dissolve. After drying at 120° C., the residue may be weighed, when its weight, multiplied by ·7402, gives that of the lactic acid. Paralactate of zinc dissolves readily in alcohol, so the above process is useless for the determination of paralactic acid. With ordinary lactic acid it yields fair approximate results, with careful manipulation and under favourable circumstances.

966. A method of determining lactic acid described by Chapman and Smith (*Jour. Chem. Soc.*, xx. 173) is based on the fact that, when heated with sulphuric acid and bichromate of potassium, lactic acid is decomposed thus:—$C_3H_6O_3 + O = C_2H_4O + H_2O + CO_2$. Hence, one-third of the carbon of the lactic acid is evolved as carbon dioxide gas. The process is conducted as follows:—A flask, having a side-tubulure, is connected by the latter with a small bulb-apparatus filled with concentrated sulphuric acid and immersed in cold water. The bulb-apparatus is connected with bulbs containing potash-solution (specific gravity 1·27), and beyond is a small tube containing fragments of caustic potash. The neck of the flask is closed by a perforated cork, through which is passed the stem of a tapped funnel. A weighed quantity of the lactate or solution of lactic acid is placed in the flask, and 150 c.c. of a solution, containing 100 grammes of bichromate of potassium and 125 of concentrated sulphuric acid to the litre, are introduced through the tap. The contents of the flask are then heated by hot water (not by a flame). Carbon dioxide gas is evolved, which

bubbles through the sulphuric acid (and is thus freed from aldehyde vapour), and is absorbed by the potash solution. When no more bubbles pass, air is drawn through the apparatus, and the potash apparatus is removed and weighed. Its increase in weight, corresponding to the CO_2 produced, multiplied by 2·045 gives the amount of lactic acid present. Alcohol (if not in quantity), acetic acid, sulphurous acid, and many other substances have no disturbing influence on the results.

967. **Commercial Lactic Acid** is liable to contain the following impurities:—

INORGANIC MATTERS, left on igniting the substance. Sulphuric acid and *sulphates* will be indicated on adding barium chloride to the aqueous solution of the original substance; *chlorides* by silver nitrate; salts of *calcium* by oxalate of ammonium; *zinc*, *lead*, and *iron* by diluting the liquid, nearly neutralising with ammonia, and passing sulphuretted hydrogen.

FOREIGN ORGANIC ACIDS.—Of these, the presence of *oxalic* and *tartaric* acids will be indicated by the formation of a precipitate on adding lime water to alkaline reaction, and *citric* by precipitation occurring on boiling the liquid so obtained. *Acetic* and *butyric acids* may be recognised by their respective odours on gently heating the liquid; or more exactly by the production of the fragrant odours of their respective ethyl ethers on heating the sample with alcohol and strong sulphuric acid. Ethyl lactate boils at a high temperature and has very little odour.

SARCOLACTIC ACID may be detected by the formation of a blue *precipitate* on adding cupric sulphate to the aqueous solution of the substance.

NEUTRAL ORGANIC MATTERS, may, in general, be detected by the production of a brown colour on mixing the sample with an equal bulk of cold concentrated sulphuric acid. *Glycerin* may be detected by treating the sample with a slight excess of zinc oxide and a little water, evaporating to dryness at 100°, and treating the residue with ether-alcohol. On evaporation of the solution, glycerin will be left as a sweet syrupy liquid. On treating the residue left undissolved by ether-alcohol with alcohol alone, *sugar* and *glucose* will be dissolved. Glucose and other impurities will also be recognised by the formation of a red or yellow precipitate on heating the neutralised acid with Fehling's solution.

Lactic acid should not be materially coloured when heated with a strong solution of caustic alkali, and should be wholly soluble in ether.

968. **Lactates** of the metals are all more or less soluble in water, but usually only sparingly so in the cold. All of them are

insoluble in ether. The paralactates are usually more soluble than the salts of ordinary lactic acid, and are lævo-rotary.

969. **Calcium Lactate**, $Ca''(C_3H_5O_3)_2$, is obtained in crystals containing 5 Aq., when lactic acid is neutralised with lime or chalk and the liquid concentrated. It crystallises in small white mammillated tufts, which under the microscope appear as delicate needles, some of which look like bundles bound in the centre. From acid solutions, acid lactate of calcium crystallises in radiating trimetric needles. One part of calcium lactate dissolves in 9½ parts of cold water, and in all proportions in boiling water or alcohol. Calcium paralactate requires 12½ parts of cold water for solution, and contains 4 Aq.

970. **Ferrous Lactate**, $Fe''(C_3H_5O_3)_2$, is a soluble salt crystallising in small needles with 3 Aq. The dry salt is permanent, but the solution rapidly oxidises. Ferrous lactate is not unfrequently adulterated, the substances most used for the purpose being dried ferrous sulphate, milk-sugar, and starch. A sample of "lactate of iron," examined by M. Peltier, contained 25 per cent. of ferrous sulphate and 75 per cent. of milk-sugar. *Ferrous sulphate* can be readily detected by the copious precipitate produced on treating the solution of the sample with chloride of barium. *Milk-sugar* may be detected by rendering the solution alkaline by soda, passing sulphuretted hydrogen to precipitate the iron, filtering, adding Fehling's solution to the filtrate, filtering rapidly in the cold from the sulphide of copper, and heating the filtrate, when a yellow or red precipitate of cuprous oxide will be formed if milk-sugar be present. *Starch* may be detected in the portion of the sample insoluble in cold water, by the blue colour produced on addition of solution of iodine.

971. **Lead Lactate**, $Pb''(C_3H_5O_3)_2$, is freely soluble in water, sparingly soluble in cold but readily in hot alcohol, and slightly soluble in ether. (*Glycerate* of lead is but slightly soluble in cold water.)

972. **Zinc Lactate**, $Zn''(C_3H_5O_3)_2$, crystallises from concentrated solutions in shining crusts, and from dilute solutions in four-sided prismatic needles soluble in 58 parts of cold, or 6 of boiling water, and insoluble in alcohol. The crystals contain 3 Aq., which is lost rapidly at 100° C., and above 210° C. the salt decomposes. Zinc paralactate crystallises with 2 Aq. in slender needles, which lose their water slowly at 100° C., and give off empyreumatic vapours below 150° C. The salt is soluble in 16 parts of cold water and but sparingly in cold alcohol.

973. OXALIC ACID.

French—Acide Oxalique ; Acide d'oseille.
German—Oxalsäure ; Kleesäure.

$$C_2H_2O_4 = H_2C_2O_4 = \left.\begin{array}{c} H \\ C_2O_2 \\ H \end{array}\right\} O_2 = \left\{\begin{array}{l} CO.OH \\ CO.OH. \end{array}\right.$$

Oxalic acid bears the same relation to glycol, $C_2H_4\ (OH)_2$, that acetic acid does to ethylic alcohol.

Oxalic acid occurs ready formed in various plants—notably in the *Oxalis acetosella* and in rhubarb. It is a frequent product of the decomposition of animal matters, occurring largely in diseased and occasionally in healthy urine, in certain urinary calculi, &c. It is a product of the action of nitric acid, alkaline permanganate, and other oxidising agents on various kinds of organic matter.

974. An interesting synthesis of oxalic acid, which may attain practical importance, is the reaction of carbon monoxide on caustic alkali, with production of a formate, and conversion of the latter into oxalate by increasing the temperature.

975. In commerce, oxalic acid is always produced by one of two reactions. The first is the oxidation of starch or sugar by moderately concentrated nitric acid, with subsequent separation and purification of the resultant oxalic acid by crystallisation, &c. This well-known and simple method is now replaced in practice by the curious "sawdust process." When starch, sawdust, straw, bran, or other vegetable matter is heated with caustic potash, an oxalate is formed. Wheat-bran yields 150 per cent. of its weight of crystallised oxalic acid. Soda cannot be advantageously substituted for the potash, at least entirely, but with a mixture of the two alkalies very satisfactory results are obtained. The product of the action is treated with water, and the solution treated with slaked lime. The alkalies are recovered in a caustic state, and the calcium oxalate is separated and decomposed with sulphuric acid, the resultant oxalic acid being separated by evaporation and crystallisation.

976. Oxalic acid usually occurs crystallised with two atoms of water, $C_2H_2O_4 + 2H_2O$, the crystals being monoclinic prisms having a density of 1·641 at 4° C. Exposed to dry air, or in vacuo over oil of vitriol, the crystals lose water, become opaque, and form a white powder. The acid may also be obtained anhydrous by exposure to a gentle heat (60° to 70° C.). If at once heated to 100° C. the crystals melt, and it is then much more difficult to drive off the water. By dissolving ordinary oxalic acid in 12

parts of warm concentrated sulphuric acid, and allowing the solution to stand for several days, the anhydrous acid, $H_2C_2O_4$, is deposited in transparent crystals, which on exposure to air absorb 2 Aq. and fall to powder.

Saturated solutions of oxalic acid lose acid at 100° C., and the anhydrous acid may be readily sublimed. This furnishes a convenient mode of obtaining the pure acid for analytical purposes. The acid should previously be rendered anhydrous by heating to 60° or 70° C., and the temperature of the retort must be kept as constantly as possible at 157° C. If allowed to rise to 160° C., much loss of acid occurs, and an inferior product is obtained, containing water and formic acid. The passage of a current of dry air greatly facilitates the sublimation.[1]

Oxalic acid is colourless and odourless, and completely volatile by heat without charring.

977. 100 parts of water dissolve 8 parts of crystallised oxalic acid at 10° C. and 345 parts at 90° C.

The solution has an intensely sour taste, reddens litmus strongly, and in many respects acts like a mineral acid. It is very poisonous. It decomposes carbonates, phosphates, chromates, and various other salts, including fluorspar. (Powdered oxalic acid completely decomposes common salt or calcium chloride when the mixture is heated.) Prussian blue dissolves in oxalic acid to a clear blue liquid, sometimes employed as a blue ink. Solutions of oxalic acid are permanent in the dark, but when exposed to light the acid is rapidly decomposed.

Crystallised oxalic acid dissolves readily in cold and still more readily in boiling alcohol. It is but slightly soluble in ether, and is insoluble in chloroform, benzene, or petroleum spirit.

978. Oxalic acid is not affected by boiling with moderately strong nitric or hydrochloric acid. Cold sulphuric acid has no action on it; but when oxalic acid is heated with concentrated sulphuric acid, phosphoric acid, or either of the chlorides of phosphorus, it splits up thus:—$C_2H_2O_4 = CO + CO_2 + H_2O$.

When heated with glycerin, oxalic acid yields carbonic acid at a moderate heat, and formic acid at a higher temperature. This is the method commonly employed for producing formic acid.

Chlorine combines with dry oxalic acid to form a compound of the formula $C_2H_2O_4,Cl_2$, which is split up by water into hydrochloric and carbonic acids.

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[1] Another simple method of purifying oxalic acid is to dissolve it in boiling hydrochloric acid containing 10 to 15 per cent. of real HCl. The liquid is stirred well, and then cooled quickly to get small crystals. These are washed with small quantities of cold water till but little hydrochloric acid remains in them. They are then redissolved in boiling water and recrystallised. The product so obtained is perfectly pure.

Dioxides of manganese and lead oxidise oxalic acid to carbonic acid. Auric chloride and acid solutions of permanganates react similarly. In presence of a large excess of alkali, oxalic acid is not oxidised by permanganate (*Wanklyn*).

979. Reactions of Oxalic Acid and Oxalates.

An aqueous solution of oxalic acid presents the following analytical characters:—

a. On addition of lime water or solution of calcium acetate, a white precipitate of calcium oxalate, $CaC_2O_4+H_2O$, is formed. The precipitate is very insoluble in water, and not sensibly soluble in acetic or other organic acids. It is readily soluble in dilute mineral acids. It is decomposed by boiling with excess of carbonate of sodium solution, with formation of insoluble calcium carbonate and soluble sodium oxalate. On gentle ignition, calcium oxalate evolves carbon monoxide, CO, and leaves calcium carbonate. No blackening occurs in this reaction. Solutions of soluble oxalates give the same reaction as oxalic acid with lime water or calcium acetate, and react with calcium sulphate or chloride in addition. If previously neutralised by ammonia, oxalic acid solutions are precipitated by the two latter reagents.

b. With solutions of barium, oxalic acid and oxalates react in a similar manner as with solutions of calcium, but the resultant barium oxalate is not so insoluble in water or acetic acid as the calcium salt.

c. On addition of dilute sulphuric acid and manganese dioxide, warm solutions of oxalic acid and oxalates produce effervescence, owing to the formation of carbon dioxide gas, according to the reaction $H_2C_2O_4+O=H_2O+2CO_2$. The gas may be proved to be carbon dioxide by its reaction with lime water.

d. In presence of dilute sulphuric acid, a warm solution of oxalic acid rapidly decolorises potassium permanganate. From strong solutions, the resultant carbon dioxide escapes with effervescence.

980. Determination of Oxalic Acid.

Oxalic acid may be determined with considerable accuracy by either of the following methods, the details of which may be found in most works on quantitative analysis:—

a. By precipitation as calcium oxalate. The solution should be hot and dilute, and mineral acids must be absent, or previously neutralised by ammonia. In the absence of other acids forming insoluble or nearly insoluble calcium salts (*e.g.*, sulphates, tartrates, citrates, phosphates), the solution may be exactly neutralised by ammonia, and calcium chloride added. Any phosphate may be separated by digesting the precipitate with cold dilute acetic acid. In presence of sulphates, calcium sulphate should be employed as a precipitant. It is frequently preferable to have the solution acid with acetic acid, or to precipitate the acid solution with calcium acetate, so as to avoid the co-precipitation of other calcium salts. Almost all calcium salts are soluble in acetic acid, except the oxalate, racemate, and fluoride. Racemates may be previously removed by precipitation with potassium acetate in presence of alcohol. The separation of oxalates and fluorides does not occur in practice, but, if required, the oxalate can be determined by titrating the precipitate with standard permanganate. The precipitate of calcium oxalate, however produced, is to be well washed and then treated in one of the following ways :—

1. It is dried at 100° C., and weighed as CaC_2O_4.

2. It is ignited, moistened with carbonate of ammonium, again gently ignited, and weighed as $CaCO_3$.

3. It is moistened on the filter with strong sulphuric acid, and the whole ignited again, moistened with sulphuric acid, reignited, and finally weighed as $CaSO_4$.

4. It is ignited thoroughly, and the resultant calcium oxide and carbonate titrated with standard acid.

5. The filter is placed in a beaker together with water and dilute sulphuric acid, and the liquid is titrated with standard permanganate.

Of these methods, the two last are perhaps the best, because they are the least affected by any impurity in the precipitate. Process 5 aims at the direct estimation of the oxalate, and may be applied to a precipitate containing phosphate, carbonate, or sulphate; but tartrate, racemate, and most organic salts must be absent from the precipitate.

b. By treatment with dilute sulphuric acid and manganese dioxide in a carbonic acid apparatus. This process is conducted precisely as in the valuation of a manganese ore, except that excess of manganese dioxide is used instead of excess of the oxalate. 44 parts by weight of CO_2 lost by the apparatus represent 63 of crystallised, or 45 of anhydrous oxalic acid.

c. By titration with standard permanganate. The solution of the oxalate must be free from other readily oxidisable bodies, and should be warm, dilute, and pretty strongly acidulated with sulphuric acid. The permanganate is added gradually, with constant stirring, until the liquid acquires a permanent pink tint. The permanganate is preferably standardised with pure oxalic acid. Decinormal permanganate, containing 3·162 grammes $KMnO_4$ to the litre, is a suitable strength. Each c.c. of this solution will oxidise ·0063 gramme of crystallised, or ·0045 gramme of anhydrous oxalic acid. The process can be employed for titrating a precipitate of calcium oxalate.

981. **Toxicological Examination for Oxalic Acid.**—Oxalic acid and its solutions are violently *poisonous*. The same is true of the soluble oxalates. If a very concentrated solution of free oxalic acid be taken internally, an immediate burning pain in the stomach is observed, together with cramps and drawing up of the legs, and vomiting of dark and perhaps bloody coffee-coloured matters. The patient often complains that the throat feels as if tightly bound with a cord. Bloody purging next occurs, the tongue becomes sore, and the mouth swollen and usually white. Numbness and tingling of the legs, twitchings of the face, convulsions and delirium will be more or less marked, while the circulation becomes very depressed, and respiration slow and spasmodic.

With weaker solutions, the above effects are less marked; death may be almost instantaneous, or may be postponed for a considerable time. Half an ounce is an ordinary poisonous dose, but a much smaller quantity has proved fatal.

The proper *antidote* for oxalic acid is whiting, chalk, or magnesia, suspended in a small quantity of milk.

982. *After death* from poisoning by oxalic acid, the mouth, throat, and gullet will usually be found shrivelled and easy of removal. The stomach, which is frequently contracted, often contains an intensely acid, brown, gelatinous liquid. The mucous membrane, if death be rapid, may appear soft and pale, but if death be long delayed it is usually partly blackened, other portions being intensely congested, the surface peeling off and the coats underneath being gangrenous. Throughout the whole body, except the stomach and gullet, the blood is fluid. Occasional cases are on record in which morbid appearances have been nearly or entirely absent.

In cases of poisoning by oxalic acid, supposing no antidote to have been administered, the contents of the stomach will usually be intensely acid. (Of course, *moderate* acidity is the *normal* condition.)

The urine should always be examined when poisoning by oxalic acid is suspected. It should be allowed to stand in a conical glass, the clear solution subsequently decanted, and the sediment examined under the microscope for octohedral crystals of calcium oxalate. These should be found in abundance, and may also be identified by chemical tests.

983. THE TOXICOLOGICAL DETECTION OF OXALIC ACID may be effected in the following manner:—The contents of the stomach,

if acid, are digested with warm water and strained through muslin, or, if possible, through paper. To the clarified liquid, *excess* of a solution of basic lead acetate is added, which will throw down any oxalic acid, together with colouring and other organic matter. The precipitate is washed well, suspended in water, and decomposed by a current of sulphuretted hydrogen. The liquid is again filtered, when the filtrate will probably be sufficiently pure to admit of the application of the characteristic tests for oxalic acid. Of these, the most satisfactory for toxicological purposes are the production of crystals of the free acid, and the formation of a precipitate having the properties of calcium oxalate on addition of calcium chloride and ammonia, or of calcium acetate alone.

Soluble neutral oxalates can readily be detected by the above process, but a modified method must be used if a compound of calcium or magnesium has been administered as an antidote. In such a case, the contents of the stomach should be boiled for an hour or two, without previous filtration, with a strong solution of an alkaline carbonate. The liquid is filtered from the residual carbonate of earthy-metal, acidulated with acetic acid, and then precipitated with acetate of lead as above described.

984. In toxicological investigations it must not be forgotten that oxalates occur naturally in various edible vegetables, especially in rhubarb and sorrel. Hence, if the symptoms do not indicate poisoning by free oxalic acid, a quantitative determination of the oxalate present may be necessary before concluding that death has ensued through poisoning. Free oxalic acid may be extracted from animal matters by means of alcohol, which does not dissolve oxalates; but "salt of sorrel" consists largely of tetra-oxalate of potassium, which is decomposed by alcohol into free oxalic acid and insoluble di-oxalate ($KH_3(C_2O_4)_2 = KHC_2O_4 + H_2C_2O_4$).

In cases of poisoning by free oxalic acid, the acid extracted from the stomach and intestines is chiefly uncombined, but that obtained from the liver, kidneys, heart, and urine is wholly in combination.

985. **Commercial Oxalic Acid** is not liable to intentional adulteration; nevertheless, various impurities are frequently present, owing to careless manufacture or imperfect purification.

ORGANIC MATTERS other than oxalic acid are recognised by the charring or darkening of the sample when heated, or on warming with concentrated sulphuric acid.

FIXED MINERAL IMPURITIES are left as a residue on igniting the sample in the air. If the ignited residue effervesce on addition of dilute acid, an *acid oxalate* is present in the sample. Very sensible quantities of *lead* and other heavy metals are sometimes met with.[1] *Sulphuric Acid and Acid Sulphates* are sometimes present in oxalic acid in considerable quantity. The solution of such samples gives a white precipitate of $BaSO_4$ on addition of barium chloride. The same impurities are very common in commercial ammonium oxalate.

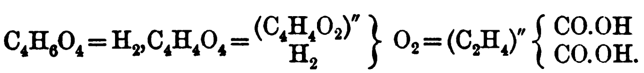
986. **Oxalates.**—These salts require but little special description. The alkali-metals form three classes of oxalates, the potassium salts having the formulæ $K_2C_2O_4,H_2O$; KHC_2O_4,H_2O; and $KH_3(C_2O_4)_2,2H_2O$. The acid salts are the least soluble. The oxalates of most other metals are insoluble, or nearly insoluble, in water. This is true of the oxalates of barium, strontium, calcium, copper, magnesium, manganese, cobalt, nickel, zinc, lead, silver, &c. The first four of these retain 1 atom of water on drying at 100°C. The remainder retain 2 atoms, with the exception of the lead and silver salts, which are anhydrous. Ferrous oxalate is but sparingly soluble, but ferric oxalate is readily so, at least in presence of free oxalic acid; hence the use of oxalic acid for removing ink-stains and dissolving Prussian blue. All the insoluble oxalates are soluble in dilute nitric acid, but they are generally insoluble in acetic acid. The determination of the oxalic acid may be readily effected by the methods described in par. 980.

On ignition, oxalates of the metals of the alkalies and alkaline-earths evolve carbon monoxide gas, and leave the corresponding carbonates. These may sometimes be further decomposed if the temperature be excessive ($CaC_2O_4 = CaO + CO + CO_2$). Oxalates of the heavy metals, when heated to redness in a close vessel, usually leave the free metal and evolve carbon dioxide gas ($NiC_2O_4 = Ni + 2CO_2$). This reaction occurs even at 100°C. in the case of gold; hence, gold is reduced from its solutions by boiling with an oxalate.

Pure oxalates do not char on ignition.

987. SUCCINIC ACID.

French—Acide Succinique. *German*—Bernsteinsäure.



$$C_4H_6O_4 = H_2,C_4H_4O_4 = \left.\begin{matrix}(C_4H_4O_2)''\\ H_2\end{matrix}\right\} O_2 = (C_2H_4)''\left\{\begin{matrix}CO.OH\\ CO.OH.\end{matrix}\right.$$

—Succinic acid occurs naturally in amber and in certain lignites; is produced during the alcoholic fermentation of sugar; and by the fermentation of malic acid and many other substances, especially under the influence of putrefying casein. Succinic acid is also produced by the action of nitric acid on the fatty acids and their glycerides, and it exists ready-formed in several plants.

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[1] In a sample of oxalic acid sold as specially purified for analytical purposes, the writer found as much as 6·3 per cent. of oxide of lead.

Succinic acid may be obtained by the dry distillation of amber, the watery distillate being filtered while hot to separate oil, when crystals of succinic acid are deposited on cooling, and may be purified by boiling with nitric acid, followed by recrystallisation from water.

988. Succinic acid bears the same relation to butylenic alcohol that oxalic acid does to ethylenic alcohol (glycol), and may be produced from butylenic alcohol by oxidation. It may also be obtained by the deoxidation of tartaric or malic acid, which contain respectively two and one atom more of oxygen than does succinic acid.

989. Succinic acid crystallises in colourless, oblique rhombic prisms or plates. When heated to 130° C. it emits suffocating fumes, and at 180° melts. When the heat is increased to 235° C. the acid boils and sublimes as succinic anhydride, $C_4H_4O_3$, which melts at 120° C. When heated strongly in the air, succinic acid burns with a blue smokeless flame.

Succinic acid is soluble in about 18 parts of cold and 0·8 boiling water. It dissolves readily in alcohol and sparingly in ether, but is insoluble in chloroform, benzene, petroleum spirit, turpentine, or carbon disulphide. Nitric acid, chlorine, and chromic acid have no action on succinic acid, and it is soluble without change in strong sulphuric acid. Permanganate has no action on a cold acid solution, but hot permanganate in presence of free alkali produces oxalic acid.

990. Reactions of Succinic Acid. In its analytical characters succinic acid somewhat resembles benzoic acid, but differs from it in not being precipitated from a strong solution of its salts by hydrochloric acid; in being precipitated by ammoniacal chloride of barium even from a dilute solution; and by being insoluble in chloroform, and therefore not removable from an acid solution by agitation with that liquid. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

Ferric chloride, if first treated with as much dilute ammonia as it will bear without precipitation, precipitates from neutral solutions of soluble succinates bulky cinnamon-brown basic ferric succinate, some free succinic acid being simultaneously produced, and the solution acquiring an acid reaction. Benzoates, under similar circumstances, gives a flesh-coloured precipitate, and cinnamates a yellow. The precipitate may be filtered off, washed, and decomposed by boiling with excess of dilute ammonia. The filtered liquid, if mixed with barium chloride and an equal bulk of alcohol, gives a white precipitate of barium succinate. By the above combination of reactions, succinic acid may be readily identified and separated from other organic acids. The process might possibly be made quantitative. For such a purpose, sodium acetate should be added to the liquid containing the iron precipitate, and the whole boiled, the precipitate produced being first boiled and then washed with dilute ammonia, the ammoniacal liquid being then concentrated and precipitated by alcohol and chloride of barium. Neutral succinates of alkali-metals may also be precipitated pretty completely by adding barium chloride to the boiling solution.

991. For the determination of the succinic acid in *wine*, I. Macagno recommends the following process:—To 1 litre of the sample add sufficient albumin or raw hide to precipitate all the tannin. The filtered liquid is concentrated and treated with hydrated oxide of lead till the colour is entirely removed. The precipitate is boiled for a long time with a 10 per cent. solution of ammonium nitrate, and the liquid filtered. The filtrate is treated with sulphuretted hydrogen, the precipitate filtered off, the filtrate concentrated to 100 c.c., and exactly neutralised with ammonia. Perfectly neutral ferric chloride is then added, the precipitate well washed, ignited, and the residual Fe_2O_3 calculated to succinic acid by multiplying the weight found by the factor 1·978.

R. Kayser concentrates 200 c.c. of the wine to one-half, adds lime-water till alkaline, filters from the precipitated calcium phosphate and tartrate, and passes carbonic acid through the filtrate. The liquid is boiled, filtered, and the filtrate precipitated by neutral ferric chloride. The precipitate is washed with alcohol of ·890 specific gravity, and ignited to ferric oxide as before.

Schmitt and Hiepe consider the above process of doubtful accuracy and recommend the one described in par. 189. Pasteur's method of determining the succinic acid in fermented liquids is described in the footnote on page 75.

Commercial Succinic Acid has usually more or less of a brown colour, and smells somewhat of the empyreumatic oil of amber, which impurity may be removed by agitation with petroleum ether. A *factitious succinic acid* has been prepared by adding a little oil of amber to tartaric acid, sal-ammoniac, or acid sulphate of potassium.

INORGANIC IMPURITIES and adulterants will be left on igniting the substance. *Cream of tartar* leaves potassium carbonate on ignition; it has been found in succinic acid to the extent of 50 per cent. *Barium sulphate* may be recognised by its insolubility and other characters; and *boric acid* by the reddish-brown colour imparted to turmeric paper, when the ash is acidulated with hydrochloric acid and the solution evaporated in contact with it. *Heavy metals* may be recognised by the usual tests.

Foreign Organic Acids may be detected by their special reactions. Thus *oxalic acid* will be precipitated on adding calcium acetate (or a mixture of calcium chloride and ammonium acetate) to the aqueous solution of the sample; *tartaric acid* by potassium acetate and alcohol; *citric acid* by the precipitate formed on adding excess of lime-water and boiling; and *benzoic acid* by its solubility in carbon disulphide or warm petroleum spirit, and by its separation on treating the precipitate produced in the neutralised liquid by ferric chloride with hydrochloric acid.

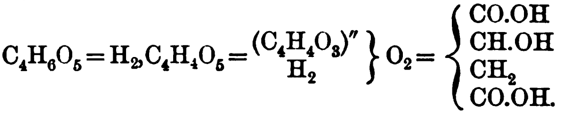
Ammonium Chloride may be recognised by the tests for ammonium salts and chlorides.

Sugar and various other impurities cause charring on warming the substance with sulphuric acid.

A useful method of examining succinic acid is to dissolve 1 gramme of the sample in 15 c.c. of hot rectified spirit, in which it should be completely soluble. When cold, one-half the solution is mixed with an equal measure of chloroform, and the other with an equal measure of ammonia. Complete admixture should occur in both cases. If the result of the test be satisfactory, and the sample leave no sensible quantity of ash, and does not notably darken with strong sulphuric acid, the substance is free from admixture.

992. MALIC ACID.

Hydroxysuccinic Acid.



$$C_4H_6O_5 = H_2C_4H_4O_5 = \left.\begin{matrix}(C_4H_4O_3)''\\ H_2\end{matrix}\right\}O_2 = \left\{\begin{matrix}CO.OH\\ CH.OH\\ CH_2\\ CO.OH.\end{matrix}\right.$$

Malic acid is contained in apples, pears, and most fruits used for domestic purposes. It is usually prepared from rhubarb stalks or mountain-ash berries.

993. Malic acid crystallises in groups of four- or six-sided prisms, which are colourless and odourless, and readily fusible. Malic acid is deliquescent and readily soluble in water, alcohol, and ether. The aqueous solution has an agreeable acid taste, and becomes mouldy on keeping. In contact with ferments, especially putrid cheese, the solution of malic acid yields succinic acid, $C_4H_6O_4$, and acetic acid, $C_2H_4O_2$. Sometimes butyric acid is produced.

994. When heated in a small retort to about 180° C., free malic acid melts and evolves vapours of maleic and fumaric acids, which crystallise on the cooler parts of the retort and receiver. Fumaric acid, $C_4H_4O_4$, forms slowly at 150° C., and mostly crystallises in the retort, in broad, colourless, rhombic or hexagonal prisms, which vaporise without melting at about 200° C., and are soluble in 250 parts of cold water, and easily in alcohol and ether. Maleic acid, $C_4H_4O_4$, is the chief product if the temperature be suddenly raised to 200° C. This body crystallises in oblique rhomboidal prisms, which melt at 130°, vaporise at about 160° C., and are readily soluble in water and alcohol. The behaviour of malic acid on heating is of value owing to the few characteristic tests for this acid.

995. Natural malic acid is lævo-rotatory in dilute solutions, optically inactive in a solution containing 34·24 per cent., and dextro-rotatory in more concentrated liquids. Artificial malic acid is inactive, but is said to be separable into two acids of opposite rotatory powers.

By the action of hydriodic acid, under pressure, malic acid is converted into succinic acid. Nitric acid and alkaline solutions of permanganate oxidise malic acid. Concentrated sulphuric acid darkens malic acid and malates very slowly on warming. When boiled with dilute sulphuric acid and bichromate of potassium, malic acid evolves an odour of ripe fruit.

996. None of the *malates* are quite insoluble in water, but few are soluble in alcohol. Solution of calcium chloride does not precipitate malic acid or malates in the cold (distinction from oxalic and tartaric acids); only in neutral and very concentrated solutions is a precipitate formed on boiling. (Citrates are precipitated from neutral boiling solutions by calcium chloride, unless the liquid be very dilute.) The addition of alcohol after chloride of calcium produces a bulky, white precipitate of calcium malate, $CaC_4H_4O_5$, even in dilute neutral solutions. Thus, if the liquid be filtered first cold (to remove oxalic and tartaric acids), and then boiling hot (to remove citric acid), the malic acid can be precipitated on addition of two volumes of alcohol. This precipitate may contain calcium sulphate or succinate, but will be free from formate,[1] acetate, benzoate, &c. On boiling the precipitate with a moderate quantity of water, the malate will be dissolved, and tannate and sulphate left almost wholly behind. The precipitate produced by calcium chloride and alcohol may also be tested for malic acid (after drying it to get rid of all trace of

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[1] If more than two volumes of alcohol be added, calcium formate may be precipitated.

alcohol) by decomposing it with dilute sulphuric acid, and boiling the filtered liquid with a *small* quantity of potassium anhydrochromate (bichromate). If the liquid remain yellow, succinic acid alone is likely to be present; but if a green colour be produced without any odour being developed, citric acid is probably present either with or without succinic acid. If the liquid acquire a green colour, and evolve an odour of ripe fruit, malic acid is present, and possibly either or both succinic and citric acid in addition.

997. Solution of acetate of lead precipitates malic acid, more perfectly after neutralisation with ammonia, as a white (and frequently crystalline) precipitate of lead malate, $PbC_4H_4O_5$, which, on boiling for a few minutes, melts under the liquid to a transparent, waxy, semi-solid. This characteristic reaction is obscured by the presence of other organic acids. The precipitate is very sparingly soluble in cold water, somewhat soluble in hot water. Malate of lead is soluble in strong ammonia, but is not readily dissolved by a slight excess. (Distinction from tartrate and citrate.) Malate of lead dissolves in ammonium acetate, and on mixing the liquid with two volumes of alcohol is reprecipitated. (Any succinate of lead remains in solution.) The precipitate of lead malate may be washed with a mixture of 2 measures of alcohol and 1 of water.

If the precipitate of malate of lead be treated with excess of ammonia, dried on the water-bath, moistened and triturated with alcoholic ammonia, and then treated with absolute alcohol, only malate of ammonium dissolves; ammonium citrate, tartrate, oxalate, &c., being insoluble in absolute alcohol. Malic acid may be separated from other organic acids in solution by adding ammonia in slight excess, and then 8 or 9 volumes of strong alcohol, which precipitates all but the malate of ammonium. The method may be conveniently applied to the solution of the free acids obtained by suspending the lead salts in water and passing sulphuretted hydrogen through the liquid.

998. If the alcoholic solution of ammonium malate be precipitated by lead acetate, and the malate of lead obtained filtered off, washed with alcohol, dried at 100° C. and weighed, the weight obtained, multiplied by 0·3953, gives the quantity of malic acid present.

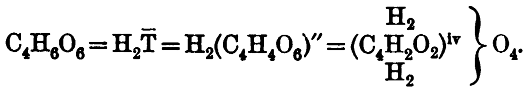
999. For the determination of malic acid in *wine*, 100 c.c. should be precipitated with a slight excess of lime water; the filtrate is concentrated to one-half its bulk, and absolute alcohol added in excess; the precipitate, consisting of calcium malate and sulphate, is collected on a filter, washed with proof spirit, dried,

and weighed. If the calcium sulphate be next determined by dissolving the precipitate in water, precipitating the solution by barium chloride, and multiplying the weight of barium sulphate obtained by ·5837, the difference may be regarded as calcium malate, 172 parts of which correspond to 134 of malic acid (see also par. 189).

R. Kayser evaporates 100 c.c. of the wine to one-half, supersaturates with sodium carbonate, adds 10 c.c. of a strong solution of barium chloride, dilutes to 100 c.c., agitates, and allows the whole to stand for twenty-four hours. The liquid is then filtered, and an aliquot portion of the filtrate acidified moderately with hydrochloric acid and evaporated to dryness at 100°. Free hydrochloric and acetic acids are volatilised, neutral chlorides and free malic acid remaining. The latter can be determined in the residue by dissolving it in water and titrating the solution with standard alkali.

1000. TARTARIC ACID.

French—Acide Tartarique. *German*—Tartarsäure, Weinsteinsäure.



$$C_4H_6O_6 = H_2\bar{T} = H_2(C_4H_4O_6)'' = \left.\begin{matrix} H_2 \\ (C_4H_2O_2)^{iv} \\ H_2 \end{matrix}\right\} O_4.$$

Tartaric acid occurs, either free or combined, in various plants. The grape is the only source from which it is commercially obtained. The deposit formed on the sides and bottom of the vessels in which wine is manufactured consists largely of calcium and potassium tartrates. After purification, it is treated with chalk and calcium sulphate, by which a nearly insoluble calcium tartrate is produced, and this, when decomposed with sulphuric acid, yields free tartaric acid, which is obtained in crystals by cooling the concentrated liquid.

1001. Tartaric acid has the constitution of a dihydroxysuccinic acid, and has been formed synthetically by boiling silver dibromsuccinate with water, or the corresponding calcium salt with lime water. $Ag_2C_4H_2Br_2O_4 + 2H_2O = 2AgBr + C_4H_6O_6$.

1002. Five distinct modifications of tartaric acid exist. Their chief physical and chemical differences are as follow:—

a. Dextro-tartaric, or Ordinary Tartaric Acid, forms anhydrous, hemihedral, rhombic crystals, the aqueous solution of which turns the plane of polarisation of a luminous ray to the ***right***, the value for S_D at 16° C. being 13°·1 for a 15 per cent., and 14°·7 for a 2 per cent. solution. The crystals fuse at 135° C., have a density of 1·74 to 1·76, and are readily soluble in absolute and in aqueous alcohol.

In the following article, ordinary tartaric acid and its salts are always referred to unless some special prefix is employed.

b. LÆVO-TARTARIC, or ANTI-TARTARIC ACID, forms anhydrous, hemihedral, rhombic crystals, the aqueous solution of which turns the plane of polarisation of a luminous ray to the *left*, the rotation being equal and opposite to that produced by dextro-tartaric acid. It ferments less readily than dextro-tartaric acid, and forms no crystalline compound with asparagine.

c. PARA-TARTARIC, or RACEMIC ACID, occurs with ordinary tartaric acid in crude tartars. It forms hydrated, holohedral, triclinic crystals containing 1 Aq., which are optically *inactive*, have a density of 1·69, effloresce in the air, and become completely anhydrous at 100°; the resultant anhydrous acid melts at about 200° C. Racemic acid is soluble in five parts of cold water, and with difficulty in cold alcohol. The calcium racemate is less soluble in water than calcium dextro-tartrate, and is also distinguished by its insolubility in acetic acid, and in chloride of ammonium solution.[1]

d. INACTIVE, or MESO-TARTARIC ACID is produced by prolonged heating of dextro-tartaric acid to 165° with a small proportion of water. It is optically inactive, but is not resolvable in *a.* and *b.* acids. Meso-tartaric acid is very soluble in water, forms crystals containing 1 Aq., and yields calcium and hydrogen-potassium salts more soluble than the corresponding salts of ordinary tartaric acid.

e. META-TARTARIC ACID is produced by fusing ordinary tartaric acid at 180° C. It is deliquescent and uncrystallisable. Its dilute solution and those of its salts are converted by boiling into those of the ordinary modification of tartaric acid. The same change occurs slowly in the cold. On the other hand, dextro-tartaric acid undergoes partial conversion into meta-tartaric acid by concentrating its solution on the water-bath.

1003. When heated to 205° C., tartaric acid loses the elements of water, and is converted successively into substances of the formulæ:—$C_8H_{10}O_{11}$; $C_4H_4O_5$; and $C_5H_8O_4$. It ultimately carbonises and emits a smell resembling that of burnt bread or sugar.

1004. Dextro-tartaric acid is soluble in 0·7 parts of cold and 0·5 parts of boiling water; in 2·5 parts of rectified spirit or 3·6 of absolute alcohol; in 250 parts of absolute ether, and is nearly insoluble in chloroform, benzene, and petroleum spirit.

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[1] Racemic acid can be prepared by mixing *a.* and *b.* tartaric acids, and can be resolved into them by appropriate methods. According to Staedel, crystal of natural racemic acid differ from the artificial product by not disintegra on exposure to air. Anhydrous artificial racemic acid is stated to fuse at 1 and the natural at 201° C.

The following table by H. Schiff shows the density of aqueous solutions of tartaric acid:—

Percentage by weight of tartaric acid.	Density at 15° C. (= 59° F.)
33	1·1654
22	1·1062
14·67	1·0690
11	1·0511
7·33	1·0337
3·67	1·0167

Aqueous solutions of tartaric acid (especially when dilute) gradually decompose with growth of fungus. The change may be prevented by the addition of a little carbolic acid. Cream of tartar and other tartrates decompose when kept in a moist state.

1005. Most oxidising agents convert tartaric into formic acid. Ammonio-silver nitrate is reduced with formation of carbonic and oxalic acids. In dilute solution, tartaric acid reduces auric and platinic chlorides, and converts mercuric chloride into calomel.

1006. Detection and Determination of Tartaric Acid and Tartrates.

a. Tartaric acid and tartrates are charred when heated with concentrated sulphuric acid of 1·845 specific gravity. The reaction may be used to distinguish a tartrate from a citrate, or to detect tartaric acid in presence of citric acid. For this purpose, 1 gramme of the sample should be treated with 10 c.c. of pure concentrated sulphuric acid (free from nitrous compounds), and the mixture heated to 100° C. for forty minutes. Citric acid gives only a yellow colour when thus treated, but if 1 per cent. of tartaric acid be present the liquid has a distinct brown shade, and this becomes still more marked with larger proportions.

b. If a drop of ferrous sulphate solution be added to a solution of tartaric acid or a soluble tartrate, then a few drops of hydrogen peroxide, and the mixture finally treated with excess of caustic soda, a fine violet coloration is produced, which in strong solutions is so deep as to appear almost black. The colour is discharged by sulphurous acid. If potassium ferrocyanide be added to the violet liquid, and then sufficient dilute sulphuric acid to acidify the solution, the iron may be filtered off and a colourless filtrate obtained which again gives the violet colour on addition of a ferrous salt. The colourless filtrate reduces salts of silver and mercury, and bichromate of potassium, and instantly decolorises permanganate. After adding excess of alkali it precipitates cuprous oxide from

Fehling's solution in the cold, and on heating metallic copper is separated.

Acidulated permanganate or sodium hypochlorite may be substituted for the hydrogen peroxide in the foregoing test, if care be taken to avoid excess, but the result is not so good as with the peroxide. Heavy metals and oxidising agents must be absent. Citric, malic, succinic, oxalic, and acetic acids and sugar were found by H. J. H. Fenton, the observer of the reaction, to give no similar coloration (*Chem. News*, xxxiii. 190; xliii. 110).

c. Soluble tartrates in neutral solution give white calcium tartrate on addition of chloride of calcium. The precipitate is nearly insoluble in cold water; soluble in many ammoniacal salts; soluble (after washing) in a cold solution of sodium hydrate, but reprecipitated on boiling; soluble in acids (including acetic); and converted by heating with a neutral solution of cupric chloride into insoluble cupric tartrate. (Citrate of calcium yields soluble cupric citrate.) Calcium tartrate may also be conveniently examined by dissolving it in the smallest possible quantity of acetic acid, adding excess of potassium chloride solution, and stirring vigorously, when the acid tartrate of potassium will be thrown down.

d. The reducing action of tartaric acid on solutions of silver is an extremely delicate test when properly applied, but is remarkably liable to failure if the proper conditions are not carefully observed. The solution of tartaric acid, or the tartrate of alkali-metal (all other metals being first removed), is rendered acid with nitric acid, *excess* of silver nitrate added, and any precipitate filtered off. To the solution, *very dilute* ammonia is added until the precipitate at first formed is nearly redissolved. The solution is again filtered, and the filtrate heated nearly to boiling for a few minutes, when a brilliant metallic mirror will be deposited on the sides of the tube. Citric acid does not reduce silver under similar circumstances, but gives a precipitate on continued boiling.

e. Tartaric acid prevents the precipitation of many metallic solutions by alkalies, stable double tartrates being formed. For the separation of heavy metals from tartrates, sulphuretted hydrogen or sulphide of sodium must be employed, according to the metals present. The filtrate may be concentrated, and any barium, strontium, calcium, or magnesium present thrown down by boiling with carbonate of sodium. Aluminium is not separated by either of the above precipitants, but the tartaric acid can be detected and estimated in the solution without removing it.

f. The best method of determining tartaric acid by direct estimation is to precipitate it in the form of potassium-hydrogen tartrate,

$KH\bar{T}$. (For the properties of this salt, see par. 1022.) When the free acid is to be determined, either alone or mixed only with citric acid, no better process can be employed than that described in par. 1048. For the determination of tartaric acid in tartrates, and in the various natural and artificial products of tartaric acid manufactories, the processes of Warington and Grosjean, described in par. 1008 *et seq.*, are by far the best.

Tartaric acid in wine may exist in the free state, and as calcium and potassium hydrogen tartrates, and ethyl tartrate is probably often present. Its determination is described on page 82.

g. Like the corresponding salts of other organic acids, the tartrates of the light metals leave on gentle ignition a residue of carbonate or oxide of the contained metal, and by dissolving this residue in standard acid and ascertaining the amount of acid neutralised by titrating the excess with standard alkali, an accurate estimation of the metal can be effected, and, if it be known whether the tartrate was originally an acid or a neutral salt, a determination of the tartaric acid itself is obtained.

h. Tartaric acid and acid tartrates neutralise alkalies completely, and litmus affords a fairly sharp indication of the end of the reaction; but phenolphthaleïn is preferable (methyl orange is unsuitable). Hence the ordinary processes of alkalimetry are applicable to tartaric acid and tartrates.

The tartaric acid in *tartrates of organic bases* may generally be determined by precipitation as acid tartrate of potassium.

The tartrates of the alcohol radicles are unimportant. *Tartrate of ethyl* may be decomposed by heating with alcoholic potash, and the acid tartrate of potassium subsequently precipitated by adding excess of acetic acid.

1007. **Commercial Tartaric Acid** is liable to contain the same impurities as citric acid, and is examined in a similar manner (see par. 1045 *et seq.*). It is also said to have been adulterated with alum and acid sulphate of potassium, the presence of either of which would be indicated by the ash left on ignition and the formation of a notable precipitate on addition of barium chloride to the aqueous solution.

Of late the commercial value of citric acid has been several pence per lb. lower than that of tartaric acid. Hence there is a possibility of the latter acid being adulterated with citric acid, though the difference in price is not so great as to make the substitution very probable. Methods of separating tartaric acid and citric acid are described in pars. 1044 and 1048.

1008. **Tartaric Acid Liquors** are the liquids resulting from the decomposition of calcium tartrate by sulphuric acid.

They are of a very complex character, containing:—free tartaric acid; foreign organic acids; sulphuric acid, and sulphates of calcium, potassium, iron, and aluminium; phosphates; and bodies of an indefinite nature. Their analytical examination is limited to the determination of the tartaric and free sulphuric acid, with the additional estimation, in some cases, of the total organic acids.

1009. The determination of the *tartaric acid* is best effected by precipitation as the acid potassium salt. Acetate of potassium is the best reagent for pure liquors, but it is inapplicable in presence of iron or aluminium. Citrate of potassium is free from this objection, and is best employed in the following manner:—

A quantity of liquor, of 30 to 40 c.c. in volume, as cold as possible, and containing from 2 to 4 grammes of tartaric acid, is treated with a saturated aqueous solution of tripotassic citrate,[1] added drop by drop with constant stirring. As soon as the free sulphuric acid is satisfied, the precipitate begins to appear in streaks on the sides of the glass In presence of much sulphuric acid, a fine precipitate of potassium sulphate will precede the formation of the acid tartrate, but is readily distinguished therefrom. When the streaks begin to appear, 1 c.c. of citrate solution is added for every gramme of tartaric acid supposed to be present. A great excess should be avoided. Should a gelatinous precipitate be formed, the experiment is repeated with a previous addition of some citric acid. After stirring continuously for ten minutes, the precipitate is washed two or three times with 25 c.c. of a 5 per cent. solution of potassium chloride, saturated with potassium bitartrate. The precipitate is then collected on a small filter and washed with the same solution, until the acidity of the filtrate is only slightly in excess of that of the solution used for washing the precipitate. The filter and precipitate are finally transferred to a beaker, and the amount of tartaric acid present is determined by titration with standard alkali set against bitartrate of potassium, litmus or phenolphthaleïn being used as the indicator. The presence of potassium sulphate in the precipitate is of no consequence, as it has no neutralising power.

Sometimes, however, an acid citrate of potassium is dragged down by the tartrate, and this is obstinately retained. It is best got rid of by dissolving the precipitate in 50 c.c. of hot water, adding 5 grammes of potassium chloride, and cooling the liquid quickly to 15°, stirring continually, and continuing the agitation for ten minutes. This purified precipitate may be washed with the ordinary washing fluid with great ease,[2] but a correction of one-half per cent. on the tartaric acid found must be made for unavoidable loss in the process of purification.

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[1] Obtained by neutralising citric acid by pure potash or potassium carbonate.

[2] The filtrate may be tested for citric acid by neutralising it with soda, and

Under favourable circumstances, determinations by the above method show from 99 to 100 per cent. of the tartaric acid present, but much greater variations occur if the proper proportion of citrate is departed from. Grosjean concluded that, when an accurate assay of factory tartaric acid liquors was required, a preliminary series of experiments was necessary to ascertain what volume of citrate solution gave a precipitate of maximum acidity. This having been ascertained, a final experiment should be made, using the proper quantity of citrate solution, and washing the precipitate very thoroughly. In presence of much sulphuric acid, the results have a tendency to be in excess of the truth. From very old bad liquors, potassium *alum* may be precipitated on adding the citrate solution, owing to the formation of potassium sulphate and the sparing solubility of alum in solutions of that salt. When alum has been precipitated the results will be below the truth, as on washing with the potassium chloride solution a fluid is formed in which potassium bitartrate is readily soluble. If, on the other hand, an alcoholic washing liquid be substituted, the alum is retained in the precipitate, and increases the final acidity. The difficulty may be avoided by adding phosphoric acid before the citrate solution, but the filtration must be effected immediately after the stirring, or a gelatinous precipitate of aluminium phosphate may be thrown down.

1010. *Racemic acid*, if present, will be estimated as tartaric acid by the above method. *Inactive* and *meta-tartaric acids* are only imperfectly precipitated, owing to the greater solubility of their potassium salts. *Oxalic acid* has been detected in old liquors, but does not interfere with the results.

1011. The determination of the *free sulphuric acid* in tartaric acid liquors is troublesome, owing to the insolubility of potassium and calcium tartrates in alcohol, and to the occasional presence of alum. Thus, if mixed solutions of potash-alum and tartaric acid are treated with alcohol, potassium hydrogen tartrate and alum are precipitated, and the liquid contains free sulphuric acid, which was not present originally. A similar reaction occurs if sulphate of calcium be substituted for the alum. These errors are removed when the quantity of free sulphuric acid in the liquor is sufficiently great, and will occur in practice merely in the case of new liquors of bad quality. The following process is the best for the deter-

adding calcium chloride. After prolonged standing in the cold and filtration from a little calcium tartrate, the solution is boiled, when any precipitate will consist of calcium citrate.

mination of the free sulphuric acid:—From 5 to 20 c.c. of the liquor is slowly dropped into 100 c.c. of 90 per cent. alcohol, with continual stirring. (If the liquor be concentrated and of bad quality, it should be previously diluted with an equal bulk of water.) The precipitate contains sulphates, aluminium phosphate, &c. The solution is filtered after twenty-four hours, the precipitate washed with alcohol, and the filtrate precipitated with an alcoholic solution of calcium chloride. The precipitate is filtered off, slightly washed with alcohol, and ignited to destroy the tartrate. The ash is treated with strong nitric acid, the excess evaporated off, the residue treated with alcohol, and the insoluble calcium sulphate collected, ignited, and weighed (*Jour. Soc. Chem. Ind.*, ii. 340).

A useful indication of the presence of free sulphuric acid in tartaric acid liquors is obtained by treating the liquid with half its measure of a saturated aqueous solution of calcium chloride. A turbidity due to the formation of gypsum occurs immediately in a liquor containing sulphuric acid equivalent to 0·8 per cent. of brown oil of vitriol, and in five minutes when only 0·1 per cent. of oil of vitriol is present (Grosjean, *Jour. Soc. Chem. Ind.*, ii. 340).

1012. For the determination of the *total organic acids* in tartaric acid liquors, R. Warington recommends the following method (*Jour. Chem. Soc.*, xxviii. 982):—Exactly neutralise a known measure of the liquor with standard caustic alkali, evaporate to dryness, and ignite the residue at a very low temperature till the carbon is nearly consumed. Treat the ash with a known quantity of standard sulphuric acid, heat and decant, and treat the insoluble residue with more standard acid, concentrating, if necessary, to effect solution of the phosphates. Treat the mixed cold concentrated solutions with sufficient Rochelle salt ($KNa\bar{T}$) to keep any alumina in permanent solution, and then titrate the solution with standard alkali and litmus. The amount of standard sulphuric acid neutralised *by the ash* is the exact equivalent of the total organic acid in the liquor taken, and each c.c. of normal acid neutralised represents ·075 grammes of organic acid, expressed in terms of tartaric acid.

1013. **Lees; Argol; Tartar.**—These are products of the fermentation of grape juice; they consist largely of bitartrate of potassium, and are the materials from which tartaric acid and tartrates are extracted. Their formation is due to the diminished solubility of the tartrates in the alcoholic liquid produced by the fermentation.

1014. Lees is the solid matter collected from the bottom of the vessels in which the grape-juice is fermented.

Its composition is greatly altered by "plastering" the wine. This process consists in adding to the wine some "Yeso," which is essentially an impure calcium sulphate containing some carbonate. "Spanish earth," a kind of readily decomposed clay, is sometimes employed. The result is, that in plastered lees the tartrate exists chiefly as the neutral calcium, instead of the acid potassium salt, The total tartaric acid in lees is usually from 24 to 32 per cent. Lees contain from 30 to 40 per cent. of indefinite vegetable matter, the remainder being tartrates, sulphates (in plastered lees), oxide of iron, alumina, phosphoric acid, and sometimes lumps of plaster, water, &c.

1015. ARGOL, or CRUDE TARTAR, is the crystalline crust deposited on the sides of the vessels used for the fermentation. It exhibits some variety of composition, the tartaric acid ranging from 40 to 70 per cent., and being always present chiefly as acid potassium tartrate. Very low argols resemble superior lees, while first-class argols are equal to ordinary refined tartar. The term "argol" is also applied loosely to both tartar and lees. In argol, globules of sulphur are sometimes found; they are due to the sulphur burnt in the casks before introducing the wine.

1016. CREAM OF TARTAR, or REFINED TARTAR, is prepared by boiling crude tartar (argol) with water, filtering, and crystallising the salt from the clear liquid. The term "cream" of tartar is derived from the fact that during the evaporation of the liquid the salt is deposited in white crystalline crusts on the surface of the solution. Cream of tartar thus obtained consists chiefly of potassium hydrogen tartrate, $KHC_4H_4O_6$, but it always contains more or less calcium tartrate, which, though nearly insoluble in pure water, dissolves with moderate facility in a hot solution of the acid tartrate of potassium. The proportion of calcium tartrate normally present in commercial cream of tartar varies from 2 to 9 per cent., and any proportion present in excess of 10 per cent. may be considered as an adulterant (see a paper by the Author, *Analyst*, v. 114). In addition to containing calcium tartrate, commercial cream of tartar is sometimes adulterated to a considerable extent, the sulphates of potassium and calcium being occasionally used, in addition to marble, alum, and barium sulphate.

1017. Potassium hydrogen sulphate, $KHSO_4$, is sold under the name of "tartaline," and employed as a substitute for cream of tartar in baking powders, &c. It has a higher neutralising power than real cream of tartar, and hence is sometimes diluted with potato-starch, the mixture being sold as "cream of tartaraline."

1018. ASSAY OF TARTAR, ARGOL, &c.—For the *detection of adulterants* in cream of tartar, the following tests may be applied :—

a. The sample should be ignited, the residue boiled with water filtered off, washed, ignited, moistened with ammonium carbonate gently re-ignited, and weighed. The "insoluble ash" thus obtained from genuine cream of tartar consists of the calcium carbonate corresponding to the *calcium tartrate* originally present, and its weight may be calculated to its equivalent of the latter by multiplying the $CaCO_3$ by the factor 1·88. The calcium tartrate thus found should not exceed 10 per cent., or 12 per cent. at the outside. Any higher proportion is usually due to adulteration with compounds of calcium. Sophistication with *chloride of calcium* is said to have occurred, though very improbable, but there are authentic cases of adulteration by *chalk* and *marble.* The author has found 20 per cent. of *calcium sulphate* (anhydrous),[1] probably added as *plaster of Paris.* In the case of adulterated samples, the proportion of calcium tartrate cannot be deduced with accuracy from the percentage of "insoluble ash."[2]

b. The sample is boiled with a moderate excess of pure sodium carbonate and the liquid filtered. A portion of the filtrate is tested for *sulphates* (*e.g.*, calcium sulphate, potassium sulphate, and alum) by acidulating slightly with hydrochloric acid and adding barium chloride, and another for *chlorides* by rendering it acid with nitric acid, and adding silver nitrate; traces of sulphates and chlorides may be neglected. The precipitate produced by sodium carbonate should be rinsed off the filter and treated with dilute hydrochloric acid. Any insoluble residue may consist of *sand* or *barium sulphate.* Both the chemical and microscopical characters may be employed to distinguish these, and to determine whether the latter adulterant is crystalline or amorphous.

c. The presence of *alum* is indicated by the detection of a notable quantity of sulphates, with simultaneous presence of alumina in the insoluble ash. The alumina cannot be precipitated by adding ammonia to the original solution of the substance, owing to the presence of tartrate; but it may be detected by neutralising the hot solution of the sample with soda, and boiling the liquid with a little acetic acid and excess of sodium phosphate. Any aluminium present will be thrown down as phosphate, tartrates having scarcely any solvent action on the precipitate at the temperature of ebullition, and in presence of excess of phosphoric acid. Alum may be dissolved out of cream of tartar by treating the finely powdered sample with a cold, saturated, aqueous solution of potassium-hydrogen tartrate, containing 5 per cent. of potassium chloride.

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[1] This was calculated from the weight of $BaSO_4$ obtained. The total calcium was considerably in excess of the proportion corresponding to 20 per cent. of $CaSO_4$.

[2] Dr E. G. Love, in a Report to the New York State Board of Health, gives the results of his examination of twenty-seven samples of "cream of tartar." Of these, sixteen were adulterated, and from some cream of tartar was entirely absent. Starch, *terra alba,* and acid phosphate of calcium were among the adulterants found. Five samples contained upwards of 70 per cent. of *terra alba,* and in one case it reached 93 per cent

1019. The *determination of the tartaric acid* in tartar, lees, and argol may be effected by various methods, but the following processes of assay, due to R. Warington, are the most generally accurate and reliable:—

a. The tartaric acid existing as $KH\bar{T}$ is determined by titrating a hot aqueous solution of 5 grammes of the sample with standard alkali and litmus or phenolphthaleïn. Each c.c. of normal alkali required corresponds to ·150 grammes of $H_2\bar{T}$ or ·188 of $KH\bar{T}$.

b. Another portion of the sample (2 grammes) is calcined in platinum at a very low red heat.[1] The ash is dissolved in hot water, and the liquid, without filtration, treated with a moderate excess of standard acid, and the solution boiled. The excess of acid is then ascertained by titrating back with standard alkali. From the alkalinity of the tartar after ignition is subtracted the alkali required to neutralise an equal weight of the original tartar, both expressed in terms of normal alkali, when the difference is the neutralising power of the bases existing as neutral tartrates. 1 c.c of normal alkali is equivalent to 0·1131 grammes of $K_2\bar{T}$, 0·094 grammes of $Ca\bar{T}$, or 0·075 grammes of $H_2\bar{T}$ as a neutral tartrate.

c. A preferable but somewhat more tedious method, for the assay of lees and argol, is the direct estimation of the total tartaric acid by precipitation as $KH\bar{T}$, after previous decomposition of the calcium tartrate by oxalate of potassium. An amount of the powdered sample, containing about 2 grammes of tartaric acid, is placed in a beaker, and heated with a small quantity of water till thoroughly softened. A strong solution of neutral potassium oxalate is next added, in quantity sufficient to react with all the calcium salts present, and yet leave an excess of about 1½ grammes of the salt. The mixture is heated, with frequent stirring, for some time longer. The solution, which will generally be strongly acid, is now cautiously treated with solution of pure potash till almost neutral. After a little further heating, the liquid (which should not occupy more than 40 c.c.) is filtered on to a small filter. The residue is well washed, and the washings concentrated on the water-bath and added to the main solution, which is made up to about 50 c.c. A strong solution of about 2 grammes of citric acid is next added, and the solution stirred continuously during ten minutes, to facilitate precipitation of the $KH\bar{T}$. The precipitate is then washed in the manner described in par. 1009, and finally dissolved and titrated with standard alkali. Each c.c. of normal alkali equals ·150 gramme of $H_2\bar{T}$.

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[1] Complete combustion of the carbon is not to be expected. If the sample contained sulphates, 5 c.c. of solution of hydrogen dioxide should be added to the solution of the ash immediately prior to the standard acid.

This direct method of determining tartaric acid in tartars, &c., gives figures somewhat lower than those obtained by the indirect alkalimetric method, but they are accurate and more consistent with the practical results of the factory.

Metallic Tartrates.

1020. Tartaric acid contains two atoms of hydrogen replaceable by metals, and hence forms two classes of metallic salts, viz., the neutral tartrates, and the acid- or bi-tartrates. Two additional atoms of hydrogen are replaceable by alcoholic or acid radicles. Few of the metallic tartrates are readily soluble in water, and all are insoluble in alcohol. The greater number of the metallic tartrates, except tartrate of mercury, are soluble in ammonia. The tartrates of the heavy metals unite with the tartrates of the alkali metals to form stable double tartrates not decomposed on adding either a fixed alkali or ammonia. Owing to the formation of these stable double tartrates, soda and ammonia produce no precipitate in solutions of iron, copper, &c., to which a sufficiency of tartaric acid or a tartrate of alkali-metal has been previously added. The method of analysing these double tartrates, and the metallic tartrates generally, is described in par. 1006.

1021. **Potassium Tartrates.**

The most important of these salts is the Potassium Hydrogen Tartrate, Acid Potassium Tartrate, or Bitartrate of Potassium. $KH,C_4H_4O_6 = KH\bar{T}$.—This substance is the principal constituent of tartar, argol, and wine-lees, and is of importance in the free state as a source of tartaric acid, and as a form for the determination of that body.

Pure bitartrate of potassium may be conveniently prepared by dividing a solution of tartaric acid into two equal parts, neutralising one portion with potassium carbonate, and adding the other. The product may be purified by recrystallisation from hot water.

1022. Acid tartrate of potassium is a white substance forming hard, trimetric crystals. It is soluble in 240 parts of water at 10° C. (=50° F.), 180 at 20° C., and in about 15 parts of boiling water. In alcoholic liquors it is much less soluble. Thus it requires (at 15° C.) 400 parts of a spirit containing 10·5 **per cent.**

of alcohol, and 2000 parts of proof spirit (49·24 per cent. alcohol) for solution. In still stronger spirit it is practically insoluble. The presence of glucose does not affect its solubility in water or weak spirit; but the presence of certain salts and acids has great influence. This is shown by the following table by Warington, in which the effect of water containing equivalent[1] quantities of various acids is given. For comparison with them, experiments were also made with solutions containing equivalent amounts of acetic and citric acids neutralised by potash. All the experiments were made at 14° C. :—

Solvent.	Grammes of Acid or Salt in 100 c.c. of Solvent.	Grammes of $KH\bar{T}$ Dissolved by 100 c.c. of Solvent.
Water,	...	·422
Acetic acid,	·8106	·422
Tartaric acid,	1·0331	·322
Citric acid,	·8448	·546
Sulphuric acid,	·6853	1·701
Hydrochloric acid,	·5037	1·949
Nitric acid,	·8445	1·969
Potassium acetate,	1·3875	·744
Potassium citrate,	1·3966	·843

These results are of importance in the estimation of tartaric acid as $KH\bar{T}$. Clearly free mineral acids should not be present, nor any large excess of potassium acetate or citrate. On the other hand, solutions of the sulphate, nitrate, and especially the chloride of potassium have very little solvent action on the precipitated acid tartrate. Thus the solubility of the acid potassium tartrate at 12° C. is 1 part in 3213 of a 5 per cent. solution of potassium chloride, and only 1 in 4401 of a 10 per cent. solution of the same salt.

Acid tartrate of potassium dissolves many metallic oxides, forming double tartrates; tartar-emetic, $K(SbO)\bar{T}$, is a compound of this character.

Cream of tartar consists chiefly of bitartrate of potassium. Its composition and the mode of assaying it are considered in par. 1016.

When acid tartrate of potassium is treated with solution of potassium carbonate or hydrate until the liquid ceases to redden litmus paper, there results:—

1023. DIPOTASSIUM TARTRATE; Neutral Tartrate of Potassium, $K_2C_4H_4O_6 = K_2\bar{T}$. This salt forms *very soluble* monoclinic prisms. When its solution is treated with an acid, $KH\bar{T}$ is precipitated.

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[1] Not equal weights, but amounts of acid requiring equal quantities of alkali for their neutralisation.

1024. Potassium-sodium Tartrate, or Rochelle Salt, $KNa\bar{T}$ is produced by neutralising cream of tartar with soda or sodium carbonate. It forms large rhombic prisms, containing four atoms of water, and is very readily soluble. Addition of acetic acid precipitates crystalline $KH\bar{T}$. This reaction distinguishes it from the neutral sodium tartrate, $Na_2\bar{T}+2H_2O$.

1025. *Seidlitz Powders* are largely composed of Rochelle salt. There is no preparation of the sort in the British Pharmacopœia, but the dispensaries of other nations have powders of the following compositions :—

	Tartaric Acid.	Rochelle Salt.	Sodium Hydrogen Carbonate.
French, . . .	31 grains.	93 grains.	31 grains.
German, . . .	31 ,,	116 ,,	38 ,,
United States, . .	35 ,,	120 ,,	40 ,,

The preparations commonly sold in England as Seidlitz powders are of very varied composition. A normal preparation may be regarded as containing 80 grains of Rochelle salt in admixture with 40 of bicarbonate of sodium, while the white paper contains 35 grains of tartaric acid. A proportion largely employed for the blue paper is a mixture of three parts of Rochelle salt with one of sodium bicarbonate. "Double Seidlitz powders" contain about the same amounts of acid and sodium bicarbonate, together with a considerably larger quantity of Rochelle salt. Sometimes the Rochelle salt is largely, and occasionally entirely, replaced by sodium bicarbonate. Such a preparation would be of a strongly alkaline character, and notably different from Seidlitz powder of the normal composition. On the other hand, if the acid be in excess, the powder is apt to produce a turbid solution with water, owing to formation of cream of tartar.

In examining so-called Seidlitz powders, the absence of notable proportions of sulphates should be proved, as a substitution of acid potassium sulphate for tartaric acid is not unlikely to occur. Some powders receive an addition of magnesium sulphate, or a minute quantity ($\frac{1}{100}$ grain) of tartar emetic, while others are flavoured with lemon or ginger, and sweetened with sugar. Potassium chlorate is a constituent of certain patent remedies of the nature of Seidlitz powders.

1026. Potassium-ferric Tartrate. Potassio-tartrate of iron. $K_3Fe'''\bar{T}_3$.—Prepared by adding precipitated ferric hydrate to cream of tartar, and then treating with cold water. It constitutes the *Ferrum Tartaratum* of Pharmacy. The solution acidulated with hydrochloric acid should give a copious blue precipitate with the ferrocyanide, but none with the ferricyanide of potassium. It should contain 30 per cent. of Fe_2O_3, as estimated from the weight of the ash insoluble in water.

1027. **Potassium Antimonyl Tartrate**; Tartarised Antimony; Tartar-emetic. French—*Tartre Stibié.* $K(SbO)'C_4H_4O_6$.—This important remedy is prepared by mixing antimonious oxide (Sb_2O_3) with cream of tartar, and subsequently adding water, boiling, filtering, and crystallising. The crystals contain half a molecule of water. Cold water dissolves 7 per cent., and boiling water 53 per cent. of the salt; the solution has an acid reaction. *Antimonial wine* is an official solution of 40 grains of tartar-emetic in a pint of sherry.

Tartar-emetic is now extensively employed for fixing certain coal-tar colours on cotton, its value for this purpose depending on the content of antimony. It is frequently largely adulterated, the percentage of antimony being sometimes scarcely one-half of that present in the pure substance.

1028. The antimony may be conveniently determined volumetrically. The sample is dissolved in water, and bicarbonate of sodium added to the solution. Excess of a standard solution of calcium hypochlorite is then added. The excess is found by titrating back with a decinormal solution of arsenite of sodium, until a drop of the liquid ceases to give a blue colour with iodide of potassium and starch. The strength of the hypochlorite solution is found by taking a measure equal to that added to the antimony solution and titrating with arsenite as before. 1 c.c. of a solution containing 4·95 grammes of pure arsenious oxide per litre has the same reducing power as ·0060 gramme of Sb or ·0072 of Sb_2O_3.

1029. *Potassium Antimonium Oxalate*, $Sb'''K_3(C_2O_4)_3 + 6H_2O$, is now used as an adulterant of, and substitute for, tartar-emetic. It is readily soluble, does not blacken on ignition or on heating with sulphuric acid, and gives a white precipitate on adding calcium chloride to the solution previously acidified with acetic acid. The salt contains only 23·7 per cent. of Sb_2O_3.

1030. **The Tartrates of Ammonium** closely resemble the corresponding potassium salts, but are wholly volatile on ignition.

1031. **Calcium Tartrates.** The neutral tartrate, $CaC_4H_4O_6 = Ca\bar{T}$, is a natural constituent of the tartarous deposit from wine, the proportion contained being much increased if the wine has been "plastered" (see par. 190). It also constitutes the greater part of the residue obtained on treating commercial tartars with hot water. Tartrate of calcium is likewise precipitated as a crystalline powder containing 4 Aq., by adding excess of calcium chloride to a solution of neutral tartrate. It is soluble in

6265 parts of water at 15° C. (=59° F.), and in 352 parts of boiling water. Free acids and cream of tartar dissolve it readily; and hence it is frequently present in notable quantity even in purified tartars (page 443). These solutions are precipitated by ammonia, either immediately or after some time. Calcium tartrate is soluble in ammonium chloride and in cold caustic alkali, the latter solution being reprecipitated on boiling. By digestion with a hot neutral solution of cupric chloride it is converted into insoluble cupric tartrate. This reaction distinguishes it from calcium *citrate*, but the reaction fails with mixtures containing a large proportion of citrate. The tartrate differs from the *racemate* and *oxalate* of calcium by its solubility in acetic acid.

Moist tartrate of calcium, if kept warm, undergoes fermentation and forms butyracetate of calcium.

The acid tartrate of calcium is sparingly soluble; in solution it is unstable, the liquid gradually depositing crystals of the neutral salt.

1032. Calcium Racemate, $CaC_4H_4O_6 + 4H_2O$, is even less soluble in water than calcium dextro-tartrate, and is precipitated in fine needles on adding calcium sulphate to a soluble racemate, or even to a solution of free racemic acid. Calcium racemate resembles the oxalate in being insoluble in acetic acid. It dissolves in hydrochloric acid to form a solution which is at once precipitated on adding ammonia, whilst the dextro-tartrate is not precipitated till after some hours.

1033. Calcium Mesotartrate, $CaC_4H_4O_6 + 3H_2O$, forms bright, glistening crystals which dissolve in 600 parts of boiling water, and separate very gradually on cooling. Like the racemate, calcium mesotartrate is insoluble in acetic acid, but is not precipitated by adding calcium sulphate to a solution of free mesotartaric acid.

1034. The *assay* of crude calcium tartrate is best conducted, according to L. Weigert (*Zeits. Anal. Chem.*, 1884, 357), by heating 5 grammes of the sample for an hour or two at 100° C. with 30 c.c. of a 10 per cent. solution of potassium carbonate. The liquid is then filtered, and the residue thoroughly washed with hot water. The filtrate is concentrated to 5 c.c. and treated with 5 c.c. of strong acetic acid, the mixture being thoroughly agitated. 100 c.c. of rectified spirit should next be added, and the whole allowed to rest for several hours, when the liquid is filtered and the precipitate of tartar washed with about 100 c.c. of rectified spirit, or until 10 c.c. of the washings, after dilution with 20 c.c. of water, requires, for neutralisation, only one or two drops of standard alkali, of which 1 c.c. corresponds to 0·010 gramme of tartaric acid, or 0·02508 of $K\bar{H}\bar{T}$. The precipitate of tartar is dissolved in hot water and titrated with this solution, and to the quantity found

0·0165 gramme is added as a correction for solubility in the above quantities of solutions; or, if 5 grammes of the sample be employed, 0·33 per cent. of $KH\bar{T}$ must be added to the amount found.

The *carbonate* in crude calcium tartrate cannot be estimated by titration. It is best ascertained from the amount of carbon dioxide gas evolved on treatment with acid.

For further information on tartrate of calcium and the methods of determining it in tartarous deposits see par. 1018 *et seq.*

1035. **Cupric Tartrate,** $Cu''\bar{T}$, is a nearly insoluble, blue, crystalline powder, obtained by precipitating a neutral soluble tartrate by a neutral solution of cupric sulphate or chloride, or by digesting calcium tartrate with a hot neutral solution of cupric chloride. Cupric tartrate is soluble in ammonia, soda, and potash. The copper in the solutions so obtained is readily reduced to the cuprous condition when heated with glucose or other reducing agents, and hence alkaline solutions of cupric tartrate afford a valuable test for such bodies. Various methods of preparing such solutions have been proposed, but the reagent most generally employed is that known as Fehling's solution, which is fully described in par. 530 *et seq.*

1036. For the detection of a reducing substance by Fehling's solution, it is merely necessary to heat the clear and neutralised solution of the body to the boiling point with twice its measure of the cupric solution. In some cases, the reduction occurs in the cold, or on very gently warming the liquid. If a yellow or orange precipitate or turbidity of cuprous oxide, Cu_2O, be produced, a reducing substance is present.

1037. The following table shows the behaviour of various substances when their neutralised solutions are heated to boiling with Fehling's solution:—

The Cupric Solution is REDUCED by	*The Cupric Solution is* NOT REDUCED by
Carbohydrates, &c.—Dextrose, lævulose, maltose, mannitose, milk-sugar, galactose, arabinose, gallisin.	*Carbohydrates, &c.*—Mannite, dulcite, sucrose, inosite, cellulose, dextrin, arabin.
Alcohols, Phenols, &c. — Aldehyde, chloral, chloroform, valeraldehyde, resorcinol.	*Alcohols, Phenols, &c.* — Alcohol, glycerin, phenol, benzoic aldehyde, salicylic aldehyde.
Organic Acids.—Pyrogallic, gallotannic, trichloracetic.	*Organic Acids.*—Acetic, lactic, succinic, oxalic, tartaric, citric, gallic, saccharic, mucic, gluconic, lactonic, benzoic, salicylic.
Inorganic Acids.—Arsenious.	*Inorganic Acids.*—Sulphurous.

1038. CITRIC ACID.

French—Acide Citrique. *German*—Citronsäure.

$$C_6H_8O_7 = H_3, C_6H_5O_7 = \left.\begin{matrix}(C_6H_5O_4)''' \\ H_3\end{matrix}\right\} O_3 = H_3\overline{C}i.$$

Citric acid occurs in a free state in the juice of the whole genus of plants *Citrus* (order, *Aurantiaceæ*), and also in the gooseberry, cranberry, currant, tamarind, and many other fruits. The lemon, lime, and bergamot are the fruits from which it is extracted. It has also been manufactured from unripe gooseberries, which yield about 1 per cent. of their weight of citric acid, besides containing malic acid. Good lemons yield about 5½ per cent. of crystallised citric acid. Citrates of calcium and potassium are also widely distributed in the vegetable kingdom.

1039. Citric acid is prepared from lime, lemon, or bergamot juice, by neutralising the liquid with chalk, decomposing the resultant calcium citrate by an equivalent amount of sulphuric acid, and evaporating the liquid to the crystallising point.

Citric acid has been obtained synthetically by Grimaux and Adam, and also by Kekulé.

1040. Citric acid usually occurs as a crystalline powder, or in transparent colourless prisms belonging to the trimetric system. In the trade, citric acid crystals are always assumed to have the composition $2C_6H_8O_7 + H_2O$, but seventeen samples from various makers were found by Warington to contain from 8·46 to 9·35 per cent. of water, the average being 8·72 per cent.[1] This result agrees with the formula $C_6H_8O_7 + H_2O$, which requires 8·57 per cent. of water.

1041. Crystallised citric acid melts at 100° C., but the previously dehydrated acid fuses at 153°, and on further heating to about 175° decomposes into water and aconitic acid, $C_6H_6O_6$.[2] On

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[1] In determining the water in citric acid, it is necessary to dry the powdered sample for some hours at 50° to 60° C., and then gradually to raise the temperature to 100° C. Some samples lose their water much more readily than others; many samples effloresce in warm dry air.

[2] ACONITIC ACID, $H_3C_6H_3O_6$, is an unimportant acid occurring as a calcium salt in *Aconitum napellus* and other plants of the same genus. It also exists as a magnesium salt in *Equisetum fluviatile*. It is a product of the dehydration of citric acid, and is occasionally found in citric acid liquors. Aconitic acid also occurs in the juices of the sugar-cane, beet-root, and sorghum-cane.

Aconitic acid crystallises with difficulty in colourless, warty masses, or small four-sided plates, and is resolved into liquid itaconic acid, $C_5H_6O_4$, by heating to 187° C. Aconitic acid is readily soluble in water, alcohol, and ether. Anhydrous ether may be employed to separate it from citric acid. Aconitic acid crystallises more readily than maleic, and is more soluble in dry distillation, citric acid yields carbon dioxide, acetone, and the two isomeric acids, itaconic and citraconic, $C_5H_6O_4$, which bodies are also produced by heating citric acid under pressure with water or a dilute acid.

1042. Citric acid has a strong, but pleasant acid taste. Four parts of citric acid dissolve in three parts of cold, or two of boiling water, the hot saturated solution readily depositing crystals of the acid on cooling. The solution of citric acid has no rotatory action on a ray of polarised light.

Aqueous solutions of citric acid readily turn mouldy. When mixed with chalk and yeast, and exposed to a temperature of about 25° C., the solution ferments, with formation of acetate and butyrate of calcium.

Citric acid is very soluble in aqueous and in absolute alcohol, but is nearly insoluble in ether, chloroform, benzene, or petroleum spirit.

1043. When heated with syrupy phosphoric acid, citric acid gives off carbonic oxide, carbonic acid, acetone, and other products. A similar reaction occurs on heating with concentrated sulphuric acid, but sulphur dioxide is evolved in addition, and more or less colouring ensues (par. 1006, *a*). Heated with an alkali, it yields an oxalate and acetate:—$C_6H_8O_7 + 4KHO = K_2C_2O_4 + 2KC_2H_3O_2 + 3H_2O$.

When citric acid is heated with dilute sulphuric acid and manganese dioxide, or an acidulated solution of potassium permanganate, it is oxidised with formation of carbon dioxide and acetone.

Bromine and chlorine act on a solution of sodium citrate in sunlight, with formation of pentabrom- and pentachlor-acetone respectively.

1044. Detection and Determination of Citric Acid and Citrates.

water than fumaric acid (par. 994). Its aqueous solution has a decided acid reaction, and a sour taste.

Many of the aconitates are insoluble. *Mercurous aconitate* is precipitated on adding mercurous nitrate to a solution of free aconitic acid. *Aconitate of calcium*, $Ca_3(C_6H_3O_6)_2 + 6H_2O$, forms small crystals which require 100 parts of cold water for solution, but are much more soluble in boiling water. Hence aconitic acid gives no precipitate with lime water either in the cold or in boiling, a behaviour which distinguishes it from citric acid. If the solution of calcium aconitate be treated with lead acetate, insoluble *aconitate of lead* is precipitated, which, when decomposed by sulphuretted hydrogen, yields free aconitic acid.

When perfectly free from citric acid, aconitic acid does not prevent the precipitation of ferric solutions by ammonia. Citric acid may be detected in aconitic acid by converting the acid into a barium salt, and examining the crystals microscopically; barium citrate assumes very characteristic forms.

a. When 5 grammes of citric acid are heated with 30 c.c. of ammonia for six hours in a sealed tube at a temperature of 120° C.,[1] a yellow coloration is observed, and small crystals are formed. If the cooled liquid be poured into an evaporating basin, it becomes blue in the course of some hours, the colour becoming more intense on standing, and in a few days turning to green, and ultimately disappearing. The change of colour goes on more slowly in the dark. Heating the liquid on the water-bath hastens the production of the colour. Malic, tartaric, and oxalic acids do not interfere, even when present in large excess; but itaconic acid must be absent. It is said that 0·01 gramme of citric acid can be detected by this process (*Zeits. Anal. Chem.*, xvii. 73).

b. Citrate of calcium is very sparingly soluble, and less soluble in hot water than in cold. Hence, addition of excess of lime water to a solution of citric acid produces but a slight precipitate in the cold, but a somewhat more considerable precipitate of tricalcic citrate, $Ca_3\bar{C}i_2$, is obtained on boiling, the deposit redissolving as the solution cools.

Precipitation as tricalcic citrate may be employed for the determination of citric acid (see par. 1054, *d*), and serves to separate citrates from *malates, acetates, formates, butyrates, &c.;* but the precipitate may contain tartrate, oxalate, or racemate of calcium.

Citric acid may be roughly separated from tartaric acid by digesting the mixed calcium salts with a hot and perfectly neutral solution of cupric chloride,[2] when soluble cupric citrate is formed, and an insoluble tartrate remains. In the case of mixed tartrates and citrates which can be converted into the calcium salts by precipitation with calcium chloride or nitrate in perfectly neutral boiling solution, this method of separation is occasionally convenient for qualitative purposes, but it is greatly inferior to the precipitation of the tartaric acid as an acid potassium salt, and fails wholly if the proportion of tartrate be small.

c. From *tartaric acid*, citric acid is best separated by the method described in par. 1048. In the filtrate from the precipitate of acid potassium tartrate, the citric acid may be determined by boiling off the alcohol, exactly neutralising with soda, and proceeding as directed in par. 1054, *d*, or by precipitation with barium acetate or lead acetate (see *e* and *g*). If the acids do not exist in the free state, the solution must be prepared as directed under tartaric acid (see par. 1006, *e*).

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[1] This temperature is conveniently obtained by immersing the tube in a bath of boiling saturated solution of nitrate of sodium.

[2] This solution is best extemporised by precipitating a solution of cupric sulphate by barium chloride, and filtering from the resultant sulphate of barium.

d. From *oxalic acid* citric acid is separated by neutralising the solution with soda, acidifying with acetic acid, and adding calcium sulphate or chloride. After filtering from the precipitated calcium oxalate, the citric acid may be thrown down by adding lime water and boiling.

e. If moderately pure, citric acid may sometimes be conveniently converted into barium citrate, $Ba_3\bar{C}i_2$, by precipitating the neutralised solution with barium acetate, and adding two volumes of 95 per cent. alcohol. After twenty-four hours, the precipitate is filtered off, washed with alcohol of 63 per cent., ignited, moistened with sulphuric acid, again ignited, and the weight multiplied by 0·601. Alkaline acetates do not interfere, so that the method is applicable to liquids from which the tartaric acid has been separated as $KH\bar{T}$.

f. In the absence of other free acids, citric acid may be titrated with standard caustic alkali, but the end of the reaction is not very sharply indicated with either logwood, cochineal, or litmus. Carefully made litmus paper is preferable to the solution, and the alkali should be set against pure citric acid. The best indicator in titrating citric acid is phenolphthaleïn, the end-reaction being delicate and exact.

g. For the determination of citric acid in presence of heavy metals, the latter should be first removed by sulphuretted hydrogen or sulphide of sodium, and the filtered liquid rendered neutral and precipitated with excess of lead acetate. The unfiltered liquid is mixed with an equal volume of alcohol, filtered, the precipitate washed with proof spirit, and treated with ammonia. The filtrate may contain citric and tartaric acids, but will be free from sulphates, phosphates, and oxalates. When unmixed with other lead salts, citrate of lead may be suspended in water, decomposed by sulphuretted hydrogen, the liquid filtered, well boiled, and the free citric acid in the solution titrated with standard alkali and phenolphthaleïn.

Full descriptions of the methods of determining citric acid in *lemon juice*, *citric acid liquors*, &c., will be found in subsequent paragraphs.

1045. **Commercial Citric Acid** frequently contains small quantities of *calcium salts*, due to imperfect manufacture, and traces of *iron*, *lead*, and *copper* are also met with—these last being derived from the vessels used for the crystallisation and evaporation of the acid liquids.

The presence of all these impurities is indicated by igniting 5 or 10 grammes of the sample in a porcelain crucible. The ash usually varies from 0·05 to 0·25 per cent. When the proportion of ash does not exceed the latter amount, it is rarely of importance to examine it further, except for poisonous metals. The presence of lead or copper will be readily indicated by dissolving the ash in a few drops of nitric acid, diluting largely, and passing sulphuretted hydrogen.

For the detection of smaller quantities of lead, &c., as much as 50 grammes of the sample should be dissolved in ten times the weight of water, the solution nearly neutralised with ammonia, and sulphuretted hydrogen passed through the liquid.

A very fair approximative determination of the lead or copper present may be obtained by placing the solution of the ash in a tall glass cylinder standing on a white surface, and comparing the depth of tint produced by sulphuretted hydrogen with that obtained by treating an equal bulk of a very weak standard solution of lead or copper in a similar manner. If the metal present be copper, a blue colour will be observed on treating the ash with nitric acid, and the diluted solution will give a brown colour with potassium ferrocyanide.

The presence of poisonous metals in citric acid is always accidental, and the proportion present is usually extremely small (1 part in 10,000); but as lead and copper are occasionally present in dangerous amount, it is necessary to take every precaution to avoid their introduction.

1046. Many samples of citric acid contain *free sulphuric acid*, an impurity which renders the crystals deliquescent. Sulphuric acid and sulphates may be detected and estimated by acidifying rather strongly with hydrochloric acid and adding barium chloride. 233 parts of the white precipitate of $BaSO_4$ correspond to 98 of sulphuric acid (H_2SO_4).

1047. Formerly citric acid was liable to adulteration with tartaric acid, but of late the latter substance has been somewhat the more valuable, so that the tendency to any such sophistication is reversed.

If present, tartaric acid may be conveniently detected by the charring which occurs on heating the sample with concentrated sulphuric acid, as described in par. 1006, *a*. When the proportion tartaric acid in admixture with the citric acid is not too small, it may be detected by the dark colour produced, within five minutes, when 1 gramme of the sample is dissolved in 10 c.c. of a cold saturated solution of potassium bichromate.

For the detection of tartaric acid in citric acid, Vulpius dissolves 0·5 gramme of the sample in 10 c.c. of distilled water, and adds 5 drops of the solution, drop by drop, to 15 c.c. of lime water.

If the citric acid contain mere traces of tartaric acid, a distinct turbidity will be produced in a few moments, which increases on adding more of the acid solution and stirring. In this manner the presence of 1 per cent. of tartaric acid may be detected.

1048. If present in admixture with citric acid, *tartaric acid* is best determined by converting it into the nearly insoluble acid tartrate of potassium, in the following manner (A. H. Allen *Chem. News*, xxxi., 277):—Two grammes of the sample of acid are dissolved in 20 c.c. of proof spirit (made by diluting methylated spirit to a density of ·920), the solution filtered from any residue (consisting of tartrates of potassium and calcium, &c.), and made up to 45 c.c. with proof spirit. 5 c.c. of a cold saturated solution of potassium acetate in proof spirit are next added, the liquid well stirred for ten minutes. If any tartaric acid be present it will be thrown down as a crystalline precipitate of $KHC_4H_4O_6$. When the proportion is very small there may be no defined precipitate, but there will be white streaks on the sides of the vessel, in the track of the glass rod used for stirring. Two per cent. of tartaric acid in samples of citric acid can thus be detected. When more than a trace of precipitate is obtained, it is filtered off and washed with proof spirit. Rinse the precipitate from the filter with a saturated solution of potassium-hydrogen tartrate in cold water,[1] digest in the cold for a few hours, with occasional stirring, filter and wash once with proof spirit. The precipitate consists of potassium-hydrogen tartrate. It may be rinsed off the filter with boiling water into a small porcelain dish, and weighed after evaporating off the water at 100° C. (=212° F.). The weight multiplied by the factor 0·798 (or roughly, 0·8) gives the quantity of tartaric acid in 2 grammes of the sample taken. Instead of weighing the precipitate, it may be dissolved in hot water and titrated with standard alkali and litmus or phenolphthaleïn in the ordinary manner, when each c.c. of normal alkali used equals 0·150 grammes of tartaric acid in the 2 grammes of sample taken. In many respects this method is preferable to the actual weighing of the precipitate. When great accuracy is desired, a correction should be made for the solubility of the precipitate in the mother-liquor. When the foregoing directions are adhered to, an addition of 0·020 gramme to the weight of tartaric acid actually found is sufficiently near the truth.

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[1] This is necessary to get rid of any co-precipitated citrate, which in the concentrated spirituous solutions employed has a great tendency to be dragged down with the tartrate. In cold weather a very copious precipitation of an acid potassium citrate sometimes occurs, but it dissolves with facility when digested with the solution of acid tartrate of potassium.

If desired, the citric acid may be determined in the filtrate (see par. 1054, *d*).

1049. **Citric Acid Liquors.**—This term is applied to the liquors resulting in citric acid works from the treatment of the citrate of calcium with sulphuric acid. Their assay is limited to the determination of the contained citric and sulphuric acids. For this purpose the total acidity may be determined by titration with standard alkali and phenolphthaleïn, and the free sulphuric acid then estimated. By subtracting the acidity due to the latter from the total found by titration, that due to the citric acid alone is ascertained. The free sulphuric acid is determined by treating 10 or 20 c.c. of the liquor with five times its volume of strong alcohol. After twelve hours, a portion of the clear liquor is treated with more alcohol, and, if opalescence result the whole is treated in the same way. The liquid is ultimately filtered, the precipitated sulphates washed with spirit, and the filtrate precipitated with an alcoholic solution of calcium chloride. The precipitated calcium sulphate is allowed to settle completely, the supernatant liquor poured off, and the precipitate and small quantity of remaining liquor *gently warmed.* The alcohol is gradually displaced by cautious additions of small quantities of water, and, when the precipitate has become crystalline from its conversion into gypsum, alcohol is added, and the precipitate collected on a filter, washed with spirit, ignited, and weighed as $CaSO_4$. The weight multiplied by ·7206 gives the sulphuric acid (H_2SO_4) in the liquor taken.

Another method, which agrees well with the last, is to neutralise exactly a known measure of the citric liquor with pure caustic soda, evaporate to dryness, and ignite gently in platinum. The ash is wholly dissolved in a known quantity of standard acid, and the excess of acid ascertained by titration with alkali. (In presence of iron or aluminium, some neutral sodium tartrate or Rochelle salt should be added before titration.) The acid neutralised by the ash is equivalent to the organic acid contained in the liquor used.

In old liquor, the citric acid should be precipitated as calcium salt, as other organic acids will be present in serious amount. For this purpose the liquor is treated exactly as directed for juice (par. 1054, *d*).

1050. **Lemon-juice; Bergamot-juice; Lime-juice.**—These juices contain free citric acid; free acids other than citric; citrates; salts of organic acids other than citric; salts of inorganic acids; and albuminous, mucilaginous, saccharine, and other indifferent bodies. Spirit is frequently added as a preservative, and mineral acids are not uncommonly employed as adulterants. Verjuice has also been used for the purpose.

1051. J. Macagno finds that the alcoholic fermentation which takes place when freshly expressed lemon-juice is kept does not diminish the amount of citric acid present, but that this is succeeded by another fermentation during which bacteria make their appearance; this causes the citric acid to diminish and the proportion of other acids (chiefly acetic and propionic) to increase. Similarly, juice expressed from rotten fruit contains acids other than citric, sometimes to the extent of 10 per cent. of the whole.

A very pure preparation has been introduced by the Montserrat Lime Juice Company. The producers grow their own limes on the Island of Montserrat, and by care in the preparation of the juice, and proper precautions to avoid fermentation, they obtain and export a very superior product.

1052. Citric acid juices lose some of their acidity by concentration. Warington observed a loss of 3·5 per cent. of the total free acid on concentrating English-pressed juice to one-sixth of its original bulk. The loss is due, at least in part, to the presence of volatile organic acids, which, of course, exist in much smaller amount in concentrated juice. Warington found 1·25 per cent. of the total acidity of concentrated juice to be due to volatile acids. Among the latter were recognised formic, acetic, and probably propionic acids.

1053. The following table, compiled from Warington's data, shows the density, free acid, and combined organic acid (the two last expressed in terms of crystallised citric acid, $H_3\bar{C}iH_2O$) of the various citric juices commonly met with in commerce :—

	Density.	Free Acid, oz. per gallon	Combined Organic Acid, oz. per gallon.
Lime-juice—			
Raw Sicilian, . . .	...	6–9	0·85
,, English, . . .	1·04 –1·05	11–13	0·3
Concentrated . . .	1·20 –1·25	56–72	6–8
Bergamot-juice—			
Concentrated, . . .	1·22 –1·25	47–55	7–8
Lemon-juice—			
Raw, ...	1·035–1·040	10·6–13·5	0·4–0·7
Concentrated, . . .	1·28 –1·38	82–112	8–6

In the following table, due to Grosjean, are given determinations of the free acid and precipitable organic acid (both calculated as citric acid) in commercial samples of concentrated lemon and other juices :—

	Density.	Acid (reckoned as Citric Acid), oz. per gallon.		Proportion of Precipitable to 100 of Free Acid.
		Free Acid.	Total Acid Precipitable.	
Lemon-juice—				
Average of 65 samples,	1·241	62·1	61·6	99·2
Sample A, . . .	1·240	65·8	59·7	90·7
Sample B, . . .	1·235	64·9	55·7	85·8
Bergamot-juice—				
Highest, . . .	1·235	47·9	48·5	101·4
Lowest, . . .	1·235	52·3	49·9	95·4
Lime-juice—				
Sample A, . . .	1·326	108·3	99·8	92·2
Sample B, . . .	1·205	59·2	53·9	91·1
Orange-juice—				
Sample A, . . .	1·400	16·8	11·6	69·0
Sample B, . . .	1·350	11·7	8·0	68·4

From the first of these tables it will be seen that English-pressed juice contains more free and less combined acid than the raw Italian and Sicilian juices. This is probably due to the fact that the finest and ripest fruit is sent to England, while the windfalls and damaged fruit are treated locally. Concentrated lemon-juice is considered of standard quality when it contains free acid equal to 66·87 of crystallised citric acid $(C_6H_5O_7+H_2O)$ or 64 oz. of nominal acid $(2H_3\bar{C}i+H_2O)$. The Board of Trade standard for lemon-juice is a density of 1·030 (without spirit), and an acidity equivalent to 30 grains per ounce (= 11 ounces per gallon) of citric acid.

According to the British Pharmacopœia, lemon-juice should have a density of 1·039, and should contain 32½ grains of acid per ounce (= 11·9 ounces per gallon).[1]

Concentrated bergamot-juice is far less acid than lemon-juice, while concentrated lime-juice is a thick viscid fluid far exceeding the others both in density and acidity.

Lemon- and lime-juices are extensively employed as antiscorbutics. The ash of the lemon-juice has been found to contain 54 per cent. of potash and 15 per cent. of phosphoric acid; but as the proportion of mineral matter is very small, it is difficult to attribute the effects of lemon-juice to the constituents of the ash.

1054. THE ASSAY OF GENUINE JUICE is practically confined to the determination of citric acid and citrates, and for this purpose the following processes are employed:—

---

[1] According to Stoddart this density is too high for the proportion of acid.

a. Determination of the specific gravity.—A special hydrometer is sometimes used. On this "citrometer," 60 degrees correspond to a specific gravity of 1·240, so that each degree appears to be equal to 0·004 specific gravity above unity.

The valuation by specific gravity is open to many frauds. Bergamot-juice, which has a high gravity but low acidity, has been mixed with lemon-juice, and sea-water has been added to the juice during concentration. Of course the presence of alcohol materially affects the density, but its influence may be got rid of by boiling the juice and again taking the density after making up the volume to that originally employed.

b. Determination of the free acid.—This is effected by titration with seminormal caustic soda, very pale and nearly neutral litmus paper being used as an indicator. In the case of concentrated juice, 50 c.c. should be diluted to 500, and 25 c.c. to 30 c.c. of the diluted liquid employed for the titration. With unconcentrated juice, 10 c.c. or 20 c.c. may be measured out at once. In either case, the alkali is added in quantity sufficient to neutralise about $\frac{5}{6}$ths of the acid present; the liquid is then boiled for a few minutes, and when quite cold the titration is completed. The neutralising power of the alkali should be known in terms of pure citric acid. The number of grammes of citric acid contained in each c.c. of the juice, multiplied by 160, gives the ounces of free acid per gallon.

c. Determination of the citric and other organic acids in combination with bases.—This is effected by evaporating to dryness the portion of juice which has been already neutralised by soda for the determination of the free acid. The residue left on evaporation is heated gradually, and charred at a low red heat. The ignited mass is treated with water, a known volume of standard sulphuric acid added, the liquid boiled and filtered, and the excess of sulphuric acid determined in the filtrate by standard alkali. The amount of sulphuric acid neutralised by the ash is equivalent to the total organic acid of the sample, for on ignition all the salts of organic acids were converted into the corresponding carbonates. 49 parts of H_2SO_4 neutralised $= 40$ of $NaHO = 70$ of $H_3C_6H_5O_7,H_2O$, or 67 of $2H_3C_6H_5O_7,H_2O$.

The result gives the total organic acid of the juice taken, calculated as citric acid. By subtracting the amount of free citric acid, obtained by titration of the acid juice, the amount of combined citric acid is ascertained.

If the original acid juice be evaporated and ignited, and the combined citric acid calculated from the neutralising power of the ash, the results obtained are too high, owing to the decomposition of chlorides, &c., by the citric acid during evaporation.

d. Determination of the real citric acid.—Of the organic acids present in genuine lemon and similar juices, the citric is the only one of importance which forms an approximately insoluble calcium salt. Malate and aconitate of calcium are pretty freely soluble, and the same remark applies more strongly to the acetate and butyrate of calcium produced by the fermentation of citric acid juices. For the determination of the amount of insoluble calcium salt obtainable from a citric juice, R. Warington recommends the following method (*Jour. Chem. Soc.*, xxviii. 934):—15 to 20 c.c. of unconcentrated lemon-juice, or about 3 c.c. of concentrated juice (previously diluted to facilitate exact measurement), should be exactly neutralised with pure caustic soda. The solution is brought to a bulk of about 50 c.c., and heated to boiling in a salt or glycerin bath, and so much of a solution of calcium chloride added as is known to be rather more than equivalent to the total organic acids present. The whole is boiled for half an hour, and the precipitate then collected and washed with hot water. The filtrate and washings are concentrated to about 10 or 15 c.c., the solution being finally neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is collected on a very small filter, the filtrate being employed to transfer it, and the washing with hot water being reduced as much as possible. In very accurate experiments the concentration should be repeated and any further precipitate collected. The precipitates, with their filters, are then burnt at a low red heat, and the neutralising power of the ash ascertained by treatment with standard hydrochloric acid and alkali. Each c.c. of normal acid neutralised corresponds to ·070 grammes of crystallised citric acid ($H_3\bar{C}i+H_2O$). The presence of mineral acids does not interfere; oxalic or tartaric acid would render the results inaccurate. It is desirable to add peroxide of hydrogen to the solution of the ash and boil before titrating, otherwise an error may occur from the presence of sulphides.

In English-pressed lemon-juice the real citric acid is 99 per cent. of the total organic acid, but in the concentrated Sicilian juice it varies from 88 to 95 per cent. of the total. In a sample of concentrated bergamot-juice, Warington found the precipitable acid to be about 88 per cent. of the total organic acid, but a more usual proportion is 96 to 98 per cent. The method of determining the value of juice by its acidity usually, but not invariably, gives tolerably accurate results in the case of lemon- and bergamot-juice, but in lime-juice the results are commonly in excess of the truth. Of course this statement is only true of genuine juice.

e. Determination of alcohol.—This can be effected by the ordinary distillation method described in par. 163.

1055. Adulterated Lime- and Lemon-Juices are not uncommon. The production of considerable precipitates with barium chloride and silver nitrate sufficiently indicates the presence of *sulphuric* and *hydrochloric acids* respectively, pure juices containing merely insignificant traces of sulphates and chlorides.[1] Free sulphuric acid may also be determined as in citric acid liquors (see par. 1049), and both that and free hydrochloric acid by Hehner's method for the determination of mineral acids in vinegar (see par. 908).

1056. According to F. D. Scribani (*Gaz. Chim. Ital.*, viii. 284, and *Jour. Chem. Soc.*, xxxiv. 914) *nitric acid* has occasionally been used for the adulteration of lemon-juice. On concentrating such juice the nitric acid decomposes the citric acid, either wholly or partially, with formation of oxalic, acetic, and carbonic acids; so that on neutralising the juice with lime a mixture of calcium salts is obtained. To detect the nitric acid, Scribani adds to the juice an aqueous solution of ferrous chloride, strongly acidulated with pure hydrochloric acid and quite free from ferric salt. The liquid is then boiled for a few minutes, and, after cooling, tested with a thiocyanate (sulphocyanide). If the liquid contain nitric acid, a more or less deep-red colour will be produced, owing to the formation of a ferric salt. This test is said to answer equally well in presence of common salt or sulphuric or tartaric acid.[2] In boiled and dark-coloured juices dilution is necessary before the colour can be observed.

Metallic Citrates.

1057. Citric acid contains three atoms of replaceable hydrogen, and therefore forms three classes of salts. It has a great tendency to produce stable double citrates, and hence many metallic solutions are not precipitable by alkalies in presence of sufficient citric acid. This fact is often utilised in analysis.

None of the metallic citrates are wholly insoluble in water. The calcium salt is one of the least soluble and hence is employed for the determination of citric acid. Other reactions of the citrates are described in par. 1044, while the properties of the more important commercial citrates are given below.

---

[1] Sea water has been added to lemon-juice, and would, of course, react with silver nitrate.

[2] A more satisfactory and direct test for nitric acid would be to boil the juice with metallic copper, when red fumes would be produced if nitric acid were present.

1058. **Lithium Citrate.** $Li_3\bar{C}i$.—As usually prepared, this is a white powder, but it may be obtained in crystals with 4 Aq. The salt is generally stated to be deliquescent, but this is an error. It should be soluble without residue in twenty-five parts of cold water.

The pure salt, after being rendered anhydrous by drying at 115° C., on ignition leaves 52·9 per cent. of lithium carbonate, Li_2CO_3. The residue should be treated with ammonium carbonate, and again ignited very gently, as it is liable to lose carbonic acid. A higher ash than the above indicates impurity or adulteration by (probably) *sodium citrate,* which leaves 61·5 per cent. on ignition. One gramme of anhydrous lithium citrate leaves on ignition a residue which should neutralise at least 14 c.c. of normal hydrochloric acid. The same amount of sodium citrate (after ignition) would only neutralise 11·25 c.c. of acid. If the resultant solution be evaporated to dryness, lithium chloride may be dissolved out of the residue by a mixture of equal volumes of alcohol and ether, while any potassium or sodium chloride will remain undissolved.

Much of the commercial lithium citrate contains *lithium carbonate.* This gives it an alkaline reaction, and increases its has *and* its saturating power. Excess of citric acid gives the salt an acid reaction, and reduces the percentage of ash *and* the saturating power. Hence these impurities can be distinguished from sodium citrate, which *raises* the ash and *diminishes* the saturating power of the sample.

Potassium Salts may be detected by adding tartaric acid to the concentrated solution of the sample and stirring, when a white crystalline precipitate of acid tartrate of potassium will be produced.

Insoluble matters, such as powdered petalite or lepidolite, will be left undissolved on dissolving the sample in hot water, and *calcium* compounds may be estimated in the solution by adding ammonium oxalate.

1059. **Calcium Citrate.** $Ca_3C_{12}H_{10}O_{14} = Ca_3\bar{C}i_2$.—This is a white substance, very sparingly soluble in cold, and still less in hot water. It is produced, in an impure state, by the citric acid manufacturer by boiling the juice with chalk, and is sometimes offered in the market as a convenient source of citric acid. The product consists essentially of citrate mixed with other salts of calcium, and excess of chalk or lime. In Sicily, dolomitic lime is sometimes used for neutralising the juice, in which case magnesium salts will be present. It is particularly liable to decompose if the percentage of moisture is considerable (more than 10 or 12 per cent.), and therefore some samples contain scarcely any real citrate.

For the analytical examination of commercial citrate of calcium, it is sufficient to determine the citric acid and the excess of chalk or lime. For the latter purpose, 5 grammes of the sample should be dissolved in a known quantity of weak standard hydrochloric acid kept gently boiling, and, when the solution is quite cold, the amount of acid neutralised is ascertained by titration with standard alkali, as described in par. 1044, *f*. Each c.c. of normal acid neutralised by the sample corresponds to 0·050 gramme of chalk in the portion taken. To determine the organic acids, 2 grammes of the sample should be ignited, the ash boiled with standard acid, the liquid filtered and titrated with alkali. The acid neutralised by the ash is due to the chalk existing as such in the sample, *plus* the calcium carbonate produced by the ignition of the citrate and other organic salts. By subtracting the neutralisation due to the chalk proper, the equivalent of the organic acids is found; each c.c. of normal acid neutralised being equivalent to ·070 grammes of $H_3\bar{C}i,H_2O$. This method gives all the organic acids as citric acid, a result which is misleading in decomposed citrate. In such samples, the real citric acid should be determined by dissolving a known weight in hydrochloric acid, exactly neutralising with caustic soda, and treating the precipitated citrate of calcium as described in par. 1054, *d*. Citrate of magnesium, or citrate prepared with dolomitic lime, can be correctly analysed by the titration method; but if precipitation be desired, the sample must be decomposed by boiling with carbonate of sodium, the carbonate of magnesium filtered off, the filtrate neutralised with hydrochloric acid, and precipitated with calcium chloride.

1060. **Magnesium Citrate** is an intermediate form into which the citric acid of lemon-juice is sometimes converted. The popular medicine known as "Effervescent Citrate of Magnesia," is a mixture of citric and tartaric acids with acid carbonate of sodium, loaf-sugar, and about 3 per cent. of crystallised magnesium sulphate. The last constituent and the citric acid are frequently omitted. A solution sold as "citrate of magnesia" by a New York manufacturer was found by A. Claasen to contain only sodium tartrate (*Analyst*, vi. 202).

1061. **Ferric Citrate,** $Fe'''(C_6H_5O_7)'''$, is obtained by dissolving ferric oxide in citric acid and evaporating the solution in thin layers. It is thus obtained in transparent garnet-red scales, which are permanent in the air. It is insoluble in alcohol, but dissolves slowly in water to form a solution of a faintly ferruginous taste, not precipitated by ammonia, but yielding ferric hydrate on boiling with a fixed alkali. After drying at 100° C., the scales should leave from 29 to 30 per cent. of residue on ignition.

1062. Citrate of Iron and Ammonium is a preparation of the British Pharmacopœia made by dissolving precipitated ferric hydrate in a solution of citric acid and adding ammonia. It occurs in thin transparent scales of a deep red colour and slightly sweetish and astringent taste. When heated with caustic potash (*not* soda) its solution evolves ammonia and deposits ferric hydrate. The alkaline liquid filtered from the precipitate should not give any crystalline precipitate or streaks of acid *tartrate* of potassium when acidulated with acetic acid and vigorously stirred. When ignited in the air, the ammonio-citrate of iron of the British Pharmacopœia should leave not less than 27 per cent. of Fe_2O_3,[1] which should be free from alkaline reaction when moistened. Citrate of iron and ammonium is readily soluble in water, forming a faintly acid solution, but is almost insoluble in rectified spirit. A solution of 160 grains in one pint of orange wine forms the *Vinum Ferri Citras* of the British Pharmacopœia.

Citrate of Iron and Quinine will be more conveniently described under "Quinine."

1063. **Bismuth Citrate,** $Bi'''(C_6H_5O_7)'''$, is a white, amorphous, insoluble powder, obtained by boiling bismuth oxynitrate with a solution of citric acid. It is soluble in ammonia with production of the

Citrate of Bismuth and Ammonium, which occurs in small, pearly, scales, very soluble in water forming a solution which is not precipitated on dilution. The "*Liquor*" of the British Pharmacopœia has a density of 1·122, and contains 24 grains of Bi_2O_3 to the fluid ounce. The bismuth is best determined by precipitating the diluted liquid with sulphuretted hydrogen, when 1 fluid ounce should yield 26·48 grains of Bi_2S_3.

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[1] Six samples, prepared by large manufacturers of scale preparations, were found by R. Wright to yield from 31·7 to 44·0 per cent. of oxide of iron on ignition (*Pharm. Jour.* [3] xv. 731), while a specimen occurring in greenish-golden scales left only 22 per cent. The United States Pharmacopœia requires 25 per cent. of residue on ignition.

ERRATA.

Page 124, line 12, *for* "0·7174" *read* "0·7195."
Page 151, table in footnote, *for* "2·63" *read* "2·03."
Page 254, line 12, *for* "par. 692" *read* 'par. 682."

INDEX.

Absinthe, 110
Absorption spectra, 15
Acetal, 169
Acetaldehyde, 166
Acetate of aluminium, 400
—— ammonium, 395
—— amyl, 129, 158
—— calcium, 395
—— —— commercial, 395
—— copper, 402
—— ethyl, 129, 133
—— iron, 381, 400
—— —— tincture of, 401
—— magnesium, 399
—— methyl, 129
—— lead, 401
—— —— basic, solution of, 201, 402
—— potassium, 394
—— sodium, 394
Acetates, detection of, 381
—— determination of, 382
—— metallic, 394
—— reactions of, 378, 381
Acetic acid, 379
—— commercial, 385
—— density of, 379
—— detection of, 381
—— determination of, 382
—— fusing point of, 379, 387
—— furfurol in, 386
—— glacial, 379, 380, 386
—— homologues of, 404
Acetic aldehyde, 166
Acetic ether, 133
Acetone, 44, 46, 47, 381
Achro-dextrin, 347
Acids, vegetable, 377
—— fatty, 404
Aconitates, reactions of, 378
Aconitic acid, 452
Acrolein, 166
Acrylic acid, 414
Albumin, vegetable, 365
Albuminoids of cereals, 362
Alcohol, 53
—— absolute, 54
—— allylic, *see* Allyl Alcohol
—— amylic, *see* Amyl Alcohol
—— calculations, 68
—— commercial, 58
—— definition of, 41
—— density of, 54
—— density of diluted, 62
—— detection of, 59
—— —— fusel oil in, 119
—— —— methyl compounds in, 50
—— determination of, 61
—— —— by colour test, 70
—— —— by density, 61
—— —— by oxidation, 70
—— —— in tinctures, 112
—— production of, 74
—— proportion of, in wine, &c., 76
Alcoholic fermentation, 74
—— liquors, 74
Alcohols, 41
—— acid derivatives of, 377
—— hexatomic, 187
—— in fusel oil, 116
—— primary, secondary, &c., 117
Aldehyde, 166
—— acetic, 166
—— acrylic, 166
—— formic, 166
—— -resin, 168
—— trichlor-, 170
—— valeric, 160, 161, 166
Aldehydes, 163

Aldehydes, general reactions of, 164
Ale, *see* Beer
Aleurometer, 364
Algin, 350
Allyl alcohol, 44, 48
Allylene dichloride, 176
Alum, in bread, 373
—— in flour, 370, 372
Amidulin, 332
Amyl acetate, 129, 157
—— alcohol, 114
—— hydrate, 114
—— nitrate, 161
—— nitrite, 129, 158
———— commercial, 159
Amyl-sulphuric acid, 115
Amylan, 315, 344
Amylic alcohol, 114
—— deleterious effects of, 115
—— detection of, 116
———— in spirits, 119
—— determination of, 116, 121
—— separation of, from ethyl alcohol, 116, 118
Amylin, 346
Amylo-cellulose, 332
Amyloid, 318
Analysis, definition of, 1
—— elementary or ultimate, 23
Arabic acid, 351
—— gum-, 351
Arabin, 350
—— properties of, 351
Arabinose, 191, 352
Arabinosic acids, 351
Argol, 443
Arrack, 103
Arrowroot, 336, 338
Arsenic, determination of, 27
Artificial fruit essences, 162
Assay, definition of, 1
Ash, determination of, 37
—— of cereals, 367
Asparagine, 257, 367
Aspartic acid, 257

BARLEY, composition of, 361
Barley sugar, 239
Bassorin, 350, 355
Bates' saccharometer, 273
Baumé's hydrometer, 6
Beck's hydrometer, 7
Beer, 90
—— bitter substances in, 96
—— composition of, 91
—— definition of, 90
—— extract in, 93
—— glycerin in, 95
—— picric acid in, 98
—— salicylic acid in, 95
Beer-wort, original gravity of, 98
—— maltose and dextrin in, 274
—— solids in, 273
—— specific gravity of, 272
—— strength of standard, 272
Beet products, valuation of, 261
Beet-root, composition of, 260
—— juice, 260
—— molasses, 256
—— sugar, 245
Bergamot-juice, 458
Bi-rotation of sugars, 208
Black liquor, 400
Boiling points of organic bodies, 11
—— tables of, 44, 49, 117, 129, 156 160, 172, 184, 405
Brandy, 103
Bread, *see* Flour
British gum, 348
Bromide of ethyl, 129
Bromine, determination of, in organic bodies, 26
Bromoform, 184
Butyl alcohol, 117
—— chloral, 175
Butyrate of calcium, 415
—— copper, 415
—— ethyl, 129, 415
Butyric acid, 405, 406, 414
—— determination of, in wine, 410
Butyric chloral, 175
———— hydrate, 175

CAMPHOR, compound tincture of, 113
—— spirit of, 112
Cane products, valuation of, 261
Cane-sugar, 192
—— adulterations of, 251

Cane-sugar, ash of, 246
—— assay of commercial, 245
—— composition of commercial, 245
—— detection of, 242
—— determination of, 199, 242
———— in milk, 283
—— fermentation of, 74, 218
—— inversion of, 207
—— manufacture of, 244
—— optical determination of, 199
—— specific rotation of, 194
Capric acid, 406
Caproic acid, 405, 407
Caprylic acid, 406
Caramel, 239
—— in spirits, 108
Carbohydrates, density of, in solution, 209
Carbon, determination of, in organic bodies, 25
—— tetrachloride, 184
—— trichloride, 156
Cartier's hydrometer, 7
Celluloid, 329
Cellulose, 315, 316
—— determination of, 319
—— nitro-, 327
—— varieties of, 316
Cerasin, 350
Cerealin, 365
Cereals, albuminoids of, 362.
—— composition of, 361.
—— mineral constituents of, 367
Chloracetic acid, 381
Chloral, 170
—— alcoholate, 171
—— butyric or butyl, 175
—— detection and determination of, 173
—— hydrate, 171
———— assay of, 173
———— tests for purity of, 172
—— meta-, 171
—— production of, 170
Chlor-ethane, 129, 156
Chlor-ethylene, 157
Chloride of carbon, 156, 184
—— ethyl, 129, 155
—— ethylene, 157, 179
Chloride of ethylidene, 156
—— methenyl, 176
—— methyl, 129, 184
—— methylene, 183
Chlorine, determination of 26
Chlormethane, 129, 184
Chloroform, 176
—— commercial, 178
—— detection and determination of, 177
—— methylated, 180
—— spirit of, 183
Cider, 89
Citrate of barium, 453, 455
—— bismuth, 466
—— calcium, 454, 464
—— iron, 465
—— lithium, 464
—— magnesium, 465
Citrates, properties of, 463
—— reactions of, 378, 453
Citric acid, 452
—— commercial, 455
—— detection and determination of, 453, 458, 461
—— liquors, assay of, 458
—— separation of, from other acids, 454
Clerget's sugar method, 204
Cognac, 103
Collodion, 328
Compound ethers, 128
—— analysis of, 130
—— determination of, in wine, 85
—— formation of, 128
—— table of physical properties of, 129
Confectionery, sugar-, 255
Cordials, 110
Corn-cockle, in flour, 376
Cork, composition of, 322, 324
Cotton fibre, recognition of, 325
Croton chloral, 175
Crotonic acid, 175
Crystalline form of organic bodies, 3
Cutose, 322

DAMBOSE, 190
Densities, determination of, 4

Densities of saccharine solutions, 209, 212, 262
—— tables of, 44, 62, 79, 92, 99, 117, 129, 156, 160, 172, 184, 210, 212, 262
Dephlegmators, 14
Dextran, 350
Dextrin, 315, 346
—— commercial, 348
—— rotatory power of, 347
—— syrup, 348
Dextro-glucose, *see* Dextrose
Dextrose, 190, 287
—— detection and estimation of, 283, 284, 290, 300
—— specific rotatory power of, 288
Diabetic urine, examination of, 285
Diastase, preparation of, 343
Diastasic power of malt, 272, 277
Dichlorethane, 179
Di-lactic acid, 419
Dimethyl-acetal, 44, 170
Dispersion of organic bodies, 15
Distillation, 11
—— fractional, 12, 408
Draff, in malt, 271
Dulcite, 189
Dutch liquid, 157, 179

Elementary analysis of organic bodies, 23
Erythro-dextrin, 347
Erythro-mannite, 189
Essences, artificial fruit, 162
Ethylene dichloride, 157, 179
Ether, 123
—— acetic, 133
—— assay of, 125
—— chlorinated, 170
—— chloro-carbonic, 179
—— commercial, 124
—— methylated, 128
—— methylic, 127
—— nitrous, *see* Nitrous Ether
———— spirit of, 128
—— production of, 123
Ethers, compound, *see* Compound Ethers
Ethyl acetate, 133
Ethyl alcohol, *see* Alcohol
—— bromide, 129, 157
—— butyrate, 129
—— chloride, 129, 146, 155
—— chlorinated, 156
—— disulphocarbonates, 137
—— ether, 123
—— iodide, 129
—— nitrate, 129
—— nitrite, 138
———— determination of, 147
—— oxalate, 52
—— oxide, 123
—— pelargonate, 129
—— sulphates, 136
—— sulphuric acid, 137
Ethylates, 56
Ethylene chloride, 156, 179
—— -lactic acid, 418
Ethylidene chloride, 156
Eucalyn, or Eucalyptose, 191
Examination, preliminary, of organic bodies, 3
Extract, estimation of, in beer, 93
———— in wine, 80
—— of malt, 276
———— diastasic power of, 277

Fats, constitution of, 130
Fatty acids, 404
Fehling's solution, 224
—— action on different sugars, 227, 228
—— behaviour with organic bodies, 451
—— influence of conditions on reducing power of, 231
—— mode of employing, 225, 227, 451
—— preparation of, 225
—— titration of glucose by, 226
Fermentation, alcoholic, 74, 218
—— lactous, 76, 220
—— of sugar, 74, 213
Fermentative power of malt, 272
Fibres, vegetable, recognition of, 324
Fibrin, vegetable, 363
Fixed oils, constitution of, 130
Flax fibre, 325
Flour, adulterations of, 369
—— alum in, 371

Flour, ash of, 367
—— gluten in, 363
Fluorescence of organic bodies, 15
Formates, reactions of, 378, 412
Formic acid, 405, 412
—— aldehyde, 166
Formulæ, empirical, 24
Fruit essences, artificial, 162
Fumaric acid, 433
Furfurol, 165, 166
—— presence of, in acetic acid, 384, 386
Fusel oil, 116
—— assay of, 118
—— constituents of, 116
—— detection of, in spirits, 119
—— determination of, in spirits, 121

GALACTOSE, 191, 292
Gallic acid, reactions of, 378
Gallisin, 236, 237, 295, 305
Gallotanic acid, reactions of, 378
Gelose, 350
Gin, 104
Gloy, 348
Glucolignose, 321
Glucose, commercial, *see* Starch Sugar
—— dextro-, *see* Dextrose
—— lævo-, *see* Lævulose
—— syrup, 294, 298, 305
———— in honey, 311
Glucoses, 188, 190, 284
—— detection and determination of, 233, 284, 290
Glucosides, 312
Glutaminic acid, 257
Gluten, 363
—— assay of flour for, 363
Glutin or Gliadin, 363
Glyceric acid, 419
Glycerin, formation of, 75
—— determination of, in beer, 95
———— in wine, 80
Glycocine, formation of, 223
Glycogen, 315
Glycyl ethers, 130
Granulose, 332
Grape-juice, composition of, 77
Grape sugar, *see* Dextrose
Gum arabic, 351
———— assay of, 353
—— tragacanth, 350, 355
—— wood, 350
Gums, 315, 349
Gun-cotton, 330
—— nitric peroxide in, 327

HEMP fibre, recognition of, 326
Hesperidin sugar, 189
Hollands, 104
Homologues of acetic acid, 404
———— physical properties of, 405
Honey, 307
—— examination of commercial, 309
Hydracrylic acid, 419
Hydrocellulose, 317
Hydrogen, determination of, in organic bodies, 25
Hydrometers, graduation of various, 5, 273
Hydrostatic balance, 5

IMMISCIBLE solvents, use of, 30
—— behaviour of organic bodies with, 33
Inorganic matters, examination for, 37
Inosite, 191
Inulin, 315
Inversion of sugar, 207, 216
Invertin, 243
Invert sugar, 292
Iodine, determination of, in organic bodies, 26
Iodoform, 185
Iron-liquor, 400
Iso-butyric acid, 405, 414
Iso-butyl alcohol, 117
Iso-dulcite, 189
Iso-valeric acid, 405, 415
Itaconic acid, 452

JUICES, bergamot, lemon, and lime, 458
—— cane and beet, 259
Jute fibre, composition of, 324
—— recognition of, 326

KIRSCHWASSER, 104
Knapp's mercurial solution, 229

LACTATES, 421
—— reactions of, 378
Lactic acid, 418
—— commercial, 421
—— determination of, 420
—— formation of, 220
Lactic anhydride, or Lactide, 419
Lactic fermentation, 76, 220
Lactose, 191, 192, 292
Lævo-glucose (*see* Lævulose)
Lævulan, 350
Lævulin, 315
Lævulose, 199, 289
Lees, 442
Legumin, 365
Lemon and lime juice, 458
—— adulterated, 463
—— composition of, 459
Lichenin, 315
Lignin, Lignose, or Ligneous matter, 321
Linen, recognition of, 325
Liqueurs, 110

MALATE of ammonium, 434
—— barium, 435
—— calcium, 433
—— lead, 434
Malates, reactions of, 378, 433
Maleic acid, 433
Malic acid, 432
—— determination of, in wine, 83, 434
Malonic acid, 419,
Malt, 266
—— examination of, 268
—— density of solutions of, 210, 269, 272
—— extract, 276
—— liquors, *see* Beer
—— sugar, *see* Maltose
—— worts, 99, 272
Maltose, 192, 263
Mannite, 189, 289, 307
Mannitose, 191
Maraschino, 110
Meconates, reactions of, 378
Melitose, 193
Melizitose, 193
Melting points of organic bodies, 9
Mercuric solutions, reaction of sugars with, 229
Metals, determination of, in organic bodies, 27
—— detection as impurities in, 39
Metacetonic acid, 413
Metachloral, 171
Metaldehyde, 169
Metarabin, 350
Methyl acotate, 44, 46
—— alcohol (*see* Methylic Alcohol)
—— chloride, 129, 183
—— chloroform, 157
—— compounds, detection of, 50
—— ether, 127
—— iodide, 129
—— oxalate, 52
—— salicylate, 129
Methylated chloroform, 180
—— ether, 128
—— finish, 50
—— spirit, 48
———— of nitre, 155
Methylene dichloride, 183
Methylic alcohol, 41
—— detection of, 50
—— density of, 43
—— determination of, in wood spirit, 45
—— preparation of pure, 42
Milk-sugar, 192, 279
—— detection of, 234, 236
—— determination of, 236, 281
Molasses, 256
Mucedin, 363
Mucic acid, 215, 349
Mucilages, 350
Mucoid sugar, 190
Must constituents of, 77
Mycose, 193

NEUTRAL alcoholic derivatives, 123
Nitrate of amyl, 160, 161

Nitrate of cellulose, 326
—— ethyl, 129
—— sucrose, 240
Nitric acid, action of, on sugars, 214
Nitrite of amyl, 129, 158
—— ethyl, 129, 138
———— spirit of, 139
Nitrocellulose, 327
Nitrogen, determination of, in organic bodies, 25
Nitropentane, 161
Nitrosucrose, 240
Nitrous ether, 138
—— determination of, 147
—— spirit of, 139
———— assay of, 144
Normal solutions, 26
Noyeau, 111

Oat-meal, examination of, 340
Œnanthylic acid, 405, 407
Oils, constitution of fixed, 130
Opium, estimation of, in compound tincture of camphor, 113
Optical properties of organic bodies, 15
Optical saccharimetry, 199
Optically active bodies, 22
Optical rotation, 16
———— of sugars, 194
Orange juice, 460
Organic bodies, preliminary examination of, 3
—— ultimate analysis of, 23
Original gravity of worts, 98
Oxalate of antimony, 433
—— calcium, 425
Oxalates, properties of, 429
—— reactions of, 378, 425
Oxalic acid, 423
—— commercial, 428
—— determination of, 425
—— reactions of, 378, 425
—— toxicological examination for, 427
Oxycellulose, 318
Oxygen, determination of, in organic bodies, 28

Paracellulose, 317, 323
Paralactic acid, 418
Paraldehyde, 143, 169
Pararabin, 350
Parchment paper, 318
Paregoric elixir, 113
Pavy's copper solution, 228
Pectates, 322
Pectin, 350
Pectinose, 191
Pectose, 350
Pelargonates, 129, 406, 407
Pentoic acid (*see* Valeric Acid)
Peptones, in cereals, 367
Perry, 89
Persitol, 189
Phaseomannite, 191
Phosphorus, determination of, in organic bodies, 27
Physical state, changes of, 9
Picrotoxin, detection of, in beer, 96
Pinite, 189
Pith, composition of, 323
Plants, proximate analysis of, 356
Poisonous metals, examination for, 39
Polarimeters, construction of, 16
—— employment of, 202
Polarisation, circular, 16, 22
———— of sugars, 194
Potato-spirit, 114, 116
Potatoes, assay of, for starch, 345
Porter, 91, 93
Preliminary examination of organic bodies, 3
Proof spirit, 56
Propionic acid, 405, 413
—— determination of, in wine, 410
Propyl alcohol, 117
Proximate analysis of plants, 356
—— of woody tissues, 322
Pyrogallic acid, reactions of, 378
Pyroligneous acid, 384
Pyrolignite of iron, 400
—— lead, 402
—— lime, 395
Pyroxylin, 328

Quassia, detection of, in beer, 96
Quercitol, 189

Racemic acid, 436, 441, 450
Raffinose, 189

Reactions of vegetable acids, 376
Rectified spirit, 56
—— solubility of organic substances in, 34
Red liquor, 400
Reducing action of sugars, 223
—— on Fehling's solution, 224
Refraction of organic bodies, 15
Robur, 110
Rochelle salt, 448
Rotary power of sugars, 194
Rotatory power of organic bodies, 22
Rum, 105, 258
—— bay, 105
—— essence of, 129

SACCHARIC acid, 215
Saccharimetry, optical, 199
Saccharin, 222
Saccharinic acid, 222
Saccharine solutions, clarification of, 200
—— density of, 209
Saccharoids, 188, 189
Saccharometers, 213, 273
Saccharoses, 188, 192
Saccharum, 293
Sachsse's mercurial solution. 230
Salicylate of methyl, 129
Sarcolactic acid, 418
Schnapps, 104
Schweitzer's reagent, 316
Scyllite, 191
Seidlitz powders, 448
Sinodor, 399
Sizal, 326
Solidifying points of organic bodies, 9
Solvents, behaviour of organic bodies with, 30, 33, 34
Sorbinose, or sorbin, 191
Sorbite, 189
Specific gravity, 4
—— bottle, 4
—— of saccharine solutions, 209
Specific rotatory power, 20
—— of sugars, 194
—— tables of, 22, 189, 198, 236, 264, 288, 310, 315
—— of cane sugar, 194
Specific rotatory power of dextrose, 288
—— of maltose, 263
Spectra, absorption, 15
Spirit indication, 99
Spirit of camphor, 112
Spirit of nitrous ether, 139
———— analysis of, 144
Spirit of wine, 53, 56
—— methylated, 48
Spirits, 102
—— examination of, 106
—— flavouring substances in, 109
Sprengel's specific gravity tube, 5
Starch, 315, 331
—— commercial, 345
—— corpuscles, structure of, 332
—— detection of, in coffee, 341
—— determination of, 342
———— in potatoes, 345
—— isomers of, 314
—— microscopic characters of, 333
—— reaction of, with iodine, 341
—— soluble, 332
Starch sugar, 293
—— detection of, in cane sugar, 252
—— in honey, 310
Succinates, reactions of, 378, 430
Succinic acid, 429
—— commercial, 431
—— determination of, 75, 83, 431
—— formation of, 75
—— reactions of, 378, 430
Succinic anhydride, 430
Sucrates, 241
Sucro-dextrose, *see* Dextrose
Sucro-lævulose, *see* Lævulose
Sucrose, *see* Cane Sugar
Sugar, adulterations of, 251
—— beet, 245
—— cane, *see* Cane Sugar
—— commercial, 244
—— purity co-efficient of, 262
—— crystallisable in raw, 250
—— fermentation of, 213
—— grape, 287
—— invert, 292
—— inversion of, 216
—— malt, *see* Maltose
—— maple, 244

Sugar, milk, 279
—— mucoid, 190
—— solutions, clarification of, 200
———— density of, 209, 212
—— sorghum, 245
Sugar-acarus, 252
Sugar-beet, composition of the, 260
Sugar-cane, composition of the, 259
Sugar-confectionery, 255
Sugars, 187
—— action of acids on, 214, 215
———— alkalies on, 221
—— action of, as reducing agents, 223, 231
—— assay of commercial, 250
—— bi-rotation of, 208
—— classification of, 187
—— density of solutions of, 209, 212
—— inversion of, 216
—— isolation of, 194
—— non-fermentable, 189
—— recognition of various, 223
—— relations of, to polarised light, 194
—— specific rotation of, 194
———— table of, 198
—— reaction of, with Fehling's solution, 224
Sulphur, determination of, in organic bodies, 27
Sulphuric acid, action of, on sugars, 215
Sweet spirit of nitre, 140
Synanthrose, 193

TARTAR, 442
—— assay of, 443
—— cream of, 443
—— emetic, 449
Tartaline, 443
Tartaric acid, 435
—— commercial, 439
—— determination of, 437
———— in citric acid, 457
—— liquors, assay of, 439
—— reactions of, 435
—— varieties of, 435
Tartrate of ammonium, 449
—— antimony, 449
—— calcium, 449
Tartrate of copper, 451
—— potassium, 446, 447
———— and antimony, 449
———— and hydrogen, 446
———— and iron, 448
———— and sodium, 448
Tartrates, 446
—— reactions of, 378, 437
Tetrachloride of carbon, 184
Tinctures, 111
—— deposits from, 113
Tragacanth gum, 355
Tragacanthin, 350, 355
Treacle, 256
Trehalose, 193
Trichloracetic acid, 175
Trichloraldehyde, 170
Trimethylacetic acid, 4
Trinitrocellulose, 329
Twaddell's hydrometer, 6

ULMIC acid, 321
Ultimate analysis of organic bodies, 23
Urine, sugar in diabetic, 285

VALERAL, or Valeraldehyde, 161
Valerates, 416, 418
Valeric acid, 405, 415
—— commercial, 417
—— reactions of, 416
Vanillin, in molasses, 258
Vapour densities, determination of, 8
Vasculose, 321
Vegetable albumin, 365
—— acids, reactions of, 377
—— casein, 365
—— fibres, recognition of, 324
—— fibrin, 363
—— mucilages, 350
Verdigris, 403
Vinasse, 258
Vinegar, 387
—— acetic acid in, 388
—— aromatic, 390
—— cider, 389
—— -eels, 394
—— factitious, 390
—— flies in, 394
—— malt, 389

Vinegar, mineral acids in, 390
—— proof, 388
—— sugar, 389
—— sulphuric acid in, 392
—— tartaric acid in, 393
—— wine, 388
—— wood, 384
Vinous fermentation, 74
Viscose, 350

WHEAT starch, characters of, 337
—— detection of, 340
Whisky, 106
—— fusel oil in, 119
Wine, 77
—— antimonial, 449
—— alcohol in, 76
—— analysis of, 80
—— colouring matters in, 86
—— composition of, 78
—— constituents of, 77
—— ethers in, 85
—— extract in, 80
—— glycerin in, 80
Wine, malic acid in, 83
—— organic acids in, 83
—— plastering of, 84
—— propionic acid in, 410
—— salicylic acid in, 84
—— succinic acid in, 83
—— sugar in, 81
—— tannin in, 85
—— tartaric acid in, 82
—— valeric acid in, 411
—— volatile acids in, 82, 410
Wood gum, 350
—— naphtha, 44
—— spirit, 44
———— assay of, 45.
Woody tissues, analysis of, 321
—— composition of, 324
Wort, original gravity of, 98
—— strength of standard, 272

XANTHATES, 137
Xanthic acid, 137

YEAST, action of, on sugar solutions, 218

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